

# EXAMINATION OF WATER

# EXAMINATION OF WATER

## CHEMICAL AND BACTERIOLOGICAL

BY

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*SIXTH EDITION, REVISED*

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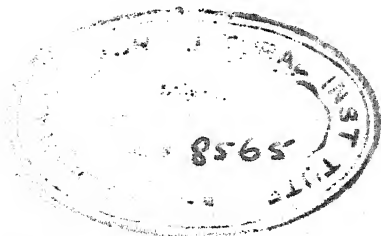
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SIXTH EDITION

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## PREFACE TO THE SIXTH EDITION

WE are sure that every student who has taken a course in water analysis has felt grateful to Professor Mason for presenting the subject in so readable and entertaining a manner as he did in the former editions of Examination of Water.

Much of the interest and charm of this little book lay in the historical background which the author was able to furnish from his own rich experience in the field. In attempting a revision it has been our aim to preserve as far as possible the spirit of the original work. Few changes have been made except where it was necessary to bring the terminology up to date. For example, the rise of chlorination of water has made it necessary to refer to the chloride ion as "chloride" rather than as "chlorine," reserving the term "chlorine" for use when the element chlorine is referred to.

The purpose of the book has always been to supply the needs of the undergraduate student rather than those of the routine analyst. For that reason considerable space has been given to the development of a setting for the various analytical tests so that the student will see them in their true perspective.

The present edition differs from the former principally in the addition of the newer analytical procedures. The methods for the determination of  $pH$  and free chlorine are notable examples. A more extensive discussion of losses due to hard water and detailed direction for the systematic analysis of boiler waters also have been included. A chapter of laboratory exercises in water treatment describes procedures whereby a student may actually carry out the



common processes of water treatment, such as softening, coagulation and chlorination. The exercise on water softening is based upon a series of tests which were a part of the routine procedure used by the Kennicott Water Softening Company to determine the cost of chemicals required for treatment. This group of exercises has been found especially useful in courses designed to instruct engineering students in the principles of water examination.

The appendix has been enlarged to include certain references not easily available to the student. We are especially indebted to Dr. Hugh S. Cumming, Surgeon General of the United States Public Health Service, for permission to include Reprint No. 1029, Drinking Water Standards, to the American Railway Engineering Association for permission to include its analytical methods, and to Dr. H. E. Howe, editor of the Technologic series of the American Chemical Society monographs, and the Chemical Catalog Company, publishers, for permission to quote from monograph No. 38. To the members of the staff of the Illinois State Water Survey the writer wishes to express his appreciation for criticism and assistance.

We regret that Professor Mason's health has not made it possible for him to actively assist in this revision. His encouragement has been a stimulation to our best effort.

A. M. BUSWELL.

URBANA, ILLINOIS,  
June, 1931

## PREFACE TO THE FIFTH EDITION

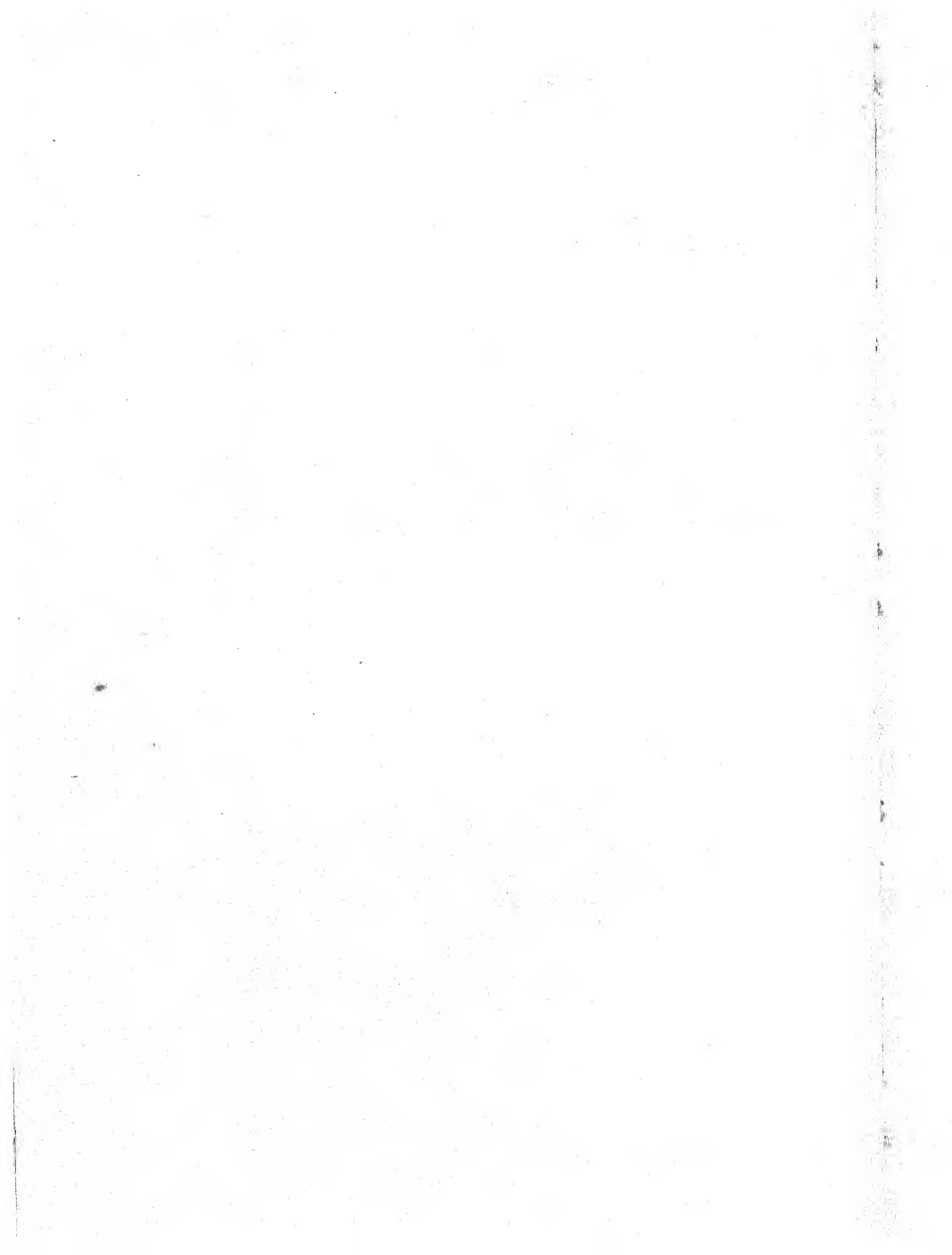
KNOWLEDGE of quantitative analysis is here necessarily assumed; therefore the merest suggestions are given for determination of the mineral matters present in a water, while the items properly lying within the scope of a sanitary examination are dealt with more at length.

Upon the bacteriological side, only so much is touched upon as has been demonstrated to be of real service to the water examiner; leaving the great field of ultimate differentiation to be further explored, and rendered still more practically useful, by the professed bacteriologist.

Sundry tests contained in former editions have been omitted and others, more suited to modern practice, have been added in their place.

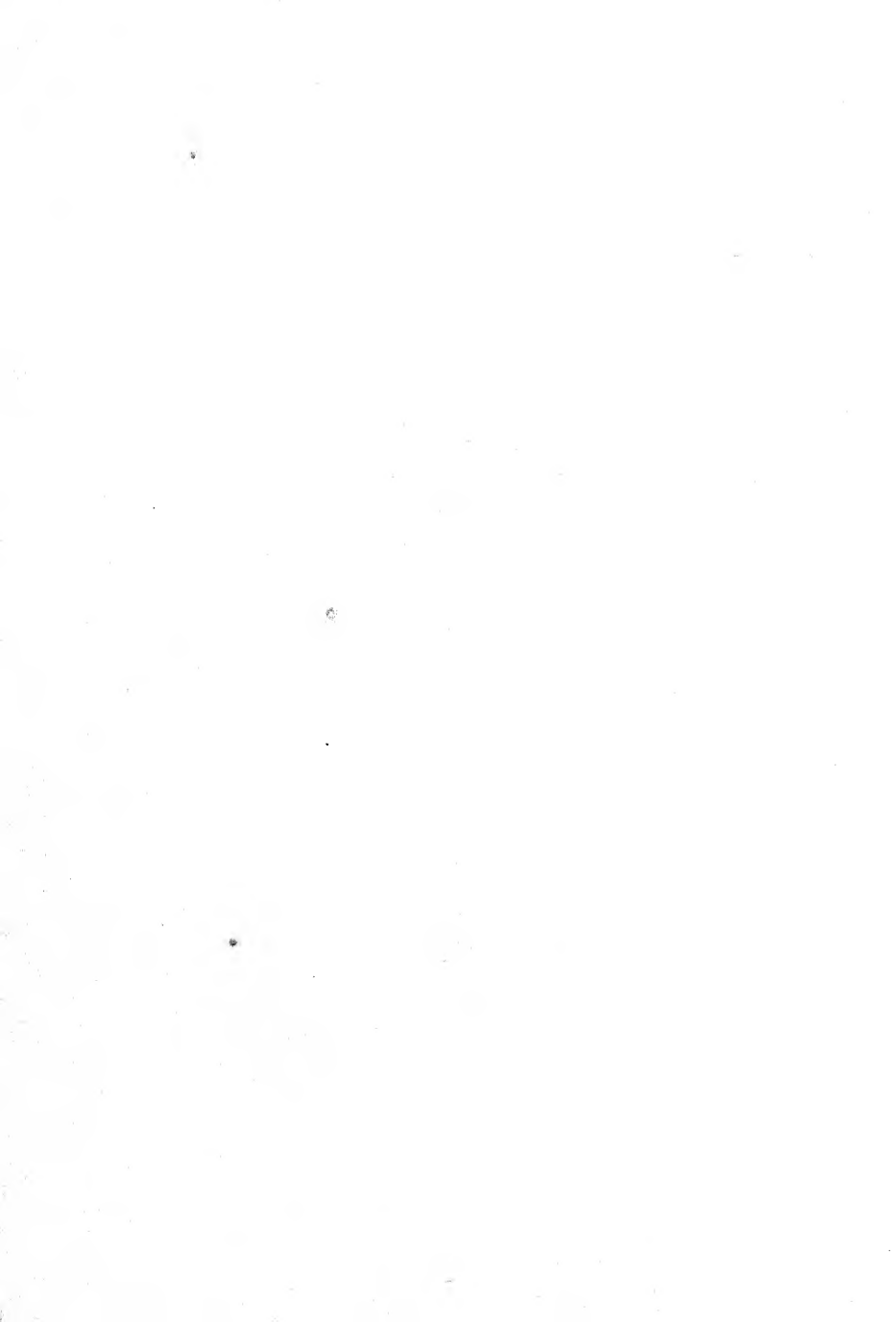
Effort has been made to place the analytical methods in harmony with the recommendations of the 1917 report of the Standard Methods Committee of the American Public Health Association, but it has been considered best not to quote directly upon too extensive a scale from that standard work, for the reason that its excellence as a book of reference interferes somewhat with its value as a working text for students' use.

RENSSELAER POLYTECHNIC INSTITUTE, TROY, N. Y.  
June, 1917



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# EXAMINATION OF WATER

## CHAPTER I

### INTRODUCTORY

A GREAT deal of popular misconception exists upon the subject of the analysis of potable water, and it is commonly supposed that such an examination may be looked upon from practically the same point of view as the analysis of an iron ore. That this belief is founded on fallacy may, however, be readily shown. When an iron ore is submitted for analysis the chemist determines and reports upon the percentages of iron, phosphorus, sulphur, etc., found therein; and at that point his duties usually cease, inasmuch as the ironmaster is ordinarily capable of interpreting the analysis for himself. Even should the analyst be called upon for an opinion as to the quality of the ore, the well-known properties of the several constituents make such a task an easy one, and, assuming the sample to have been fairly selected, the opinion may be written without any inquiry as to the nature of the local surroundings of the spot whence the ore was taken.

A water analysis, on the other hand, is really not an analysis at all, properly so called, but is a series of experiments undertaken with a view to assist the judgment in determining the potability of the supply. Although Standard Methods has been published, the manner of conducting these experiments is still largely influenced by the individual preferences of the analyst, and are far

from being uniform or always capable of comparison, thus often introducing elements of confusion where two or more chemists are employed to analyze the same water. Some of the substances reported—"albuminoid ammonia," for instance—do not exist ready formed in the water at all, and are but the imperfect experimental measures of the objectionable organic constituents which our present lack of knowledge prevents our estimating directly.

Thus the numerical results of a water analysis are not only unintelligible to the general public but are not always capable of interpretation by a chemist unless he be acquainted with the surroundings of the spot whence the sample was drawn and be posted as to the analytical methods employed.

It was formerly very common for water to be sent for analysis, with the request that an opinion be returned as to its suitability for potable uses, while at the same time all information as to its source was not only unfurnished but was intentionally withheld, with a view of rendering the desired report unprejudiced in character.

Such action was not only a reflection upon the moral quality of the chemist, but it seriously hampered him in his efforts to formulate an opinion from the analytical results.

For instance, a large quantity of common salt is a cause for suspicion when found in drinking water, not because of any poisonous property attaching to the salt itself, but because it is usually difficult to explain its presence in quantity except upon the supposition of the infiltration of sewage. Thus an amount of salt sufficient to condemn the water from a shallow well in the Hudson valley could be passed as unobjectionable if found in a deep-well water from near Syracuse, N. Y.

The writer once saw the contents of an ice-cream freezer dumped within a few feet of the mouth of a domestic well. So large an amount of salt thrown upon the ground naturally increased the quantity of chloride in the water, and

might have led to the condemnation of the well had not the source of the chloride been known.

Hence it is seen how important it is for the chemist to be fully acquainted with the history of the water he is to examine in order that he may compare his results in "chloride" with the "normal chloride" of the section whence the sample is taken.

A knowledge of the history of the water is no less important in order to interpret the remaining items of a water analysis. Some time since a water was sent from Florida to the author for examination and was found to contain 1.18 parts "free ammonia" per million. Much "free ammonia" commonly points to contamination from animal sources, and had it not been known that the water in question was derived from the melting of artificial ice made by the ammonia process the enormous quantity of ammonia found would have condemned it beyond a peradventure. As it was, the water was pronounced pure, the other items of the analysis having been found unobjectionable.

Analytical results which would condemn a surface water may be unobjectionable for water from an artesian well, for the reason that in the latter case high figures in "free ammonia," "chloride," or "nitrates" are often capable of an explanation other than that of sewage infiltration. Even though such a water should, at a previous period, have come in contact with objectionable organic waste material, yet the intervening length of time and great distance of underground flow would probably have furnished abundant opportunity for thorough purification.

"Deep" samples taken from the same lake, at the same spot and depth, will vary greatly in analytical results if the temperature of the water at the several dates of sampling should be markedly different, owing to the disturbing influence of vertical currents.

Again, suppose it is desired to determine whether or



not the water of a river is so contaminated with upstream sewage as to be unfit for a town supply. A single analysis of the water taken from the site of the proposed intake would very possibly be valueless. Examinations of any real value in such cases should always be of a comparative nature, and should extend over sufficient time to embrace seasonal and other changes common to such sources.

Thus it is that the chemist must be in full possession of all the facts concerning the water which he is asked to examine, in order that his opinion as to its purity may be based upon the entire breadth of his past experience, for in no branch of chemical work are experience and good judgment better exercised than in the interpretation of a water analysis.

A case such as this might arise: A water is condemned because of high chloride. It is completely sterilized by perfect filtration. After such filtration it contains as much chloride as before but is then pronounced as safely potable. Note how important it would be to possess a knowledge of the history of the water in such an instance.

However faithfully the various laboratory tests may be applied to decide the question of the fitness or unfitness of a certain water for dietetic purposes, there is nothing upon which greater stress should be laid than a thorough personal knowledge of the surroundings of the source of supply. In other words, it is essential to make a careful and thorough "sanitary survey."

It was years ago laid down as a golden rule "never to pass judgment upon a water the history of which is not thoroughly known," and the nearer this maxim is lived up to to-day the fewer will be the mistakes in the reports issued.

A water analysis is, for purposes of economy, rarely made complete. For ordinary drinking water the question is always asked, "Is it wholesome?" To answer this the analysis of the mineral residue left upon evaporation is not usually required, so that much time and expense may

be saved by simply reporting this as "total solids." On the other hand, analyses of mineral waters deal with this feature of the examination very largely, and usually to the exclusion of those portions, such as "albuminoid ammonia," "required oxygen," etc., which are important in sanitary analyses. The same may be said of the analyses of waters for boiler use. The development of bacteriological methods has changed though not lessened the usefulness of the chemical methods for the examination of water. The bacterial determinations give absolute data concerning the quality while the chemical tests give relative information.

The great advantage which the chemical tests possess is the rapidity with which they can be carried out. The whole series of chemical tests can be completed by an experienced analyst in three hours, while the bacterial tests require two to four days for completion.

The chemical tests find their greatest usefulness in the routine control of water-treatment plants. Suppose, for example the operator of a plant on the Great Lakes has established normal values for the various forms of nitrogen in the raw water. If the wind shifts to a quarter which is likely to increase the pollution at the intake, he can follow this increase by hourly chemical tests and adjust the operation of his plant accordingly.

## CHAPTER II

### CHEMICAL EXAMINATION OF WATER

#### DIRECTIONS FOR TAKING A WATER SAMPLE

ONE-GALLON glass-stoppered bottles are to be used for sampling. They should be most carefully cleaned, their stoppers covered with tin foil and tied down with cloth. Upon being taken to the field, they should be rinsed with the water to be sampled. Do not attempt to scour the interior of the neck by rubbing with either fingers or cloth. After thorough rinsing, fill the vessel to overflowing, so as to displace the air, completely empty it and then collect the sample.

One gallon of water is more than is needed for the analysis, but it is wise to have sufficient to guard against accidental losses.

If the water is to be taken from a tap, let enough run to waste to empty the local lateral before sampling; if from a pump, pump enough to empty all the pump connections; if from a stream or lake, take the sample well out from the shore, and sink the stoppered sampling vessel toward mid-depth before removing the stopper, so as to avoid both surface scum and bottom mud.

In every case fill the bottle nearly full, leaving but a small space to allow for possible expansion, and close securely. Under no circumstances place sealing wax upon the stopper, but tie the cloth firmly over the neck to hold the stopper in place. The ends of the string may be afterward sealed if necessary.

Stoneware jugs are not admissible for collecting water samples. They are hard to clean and some of the salt used for glazing may remain in the interior.

Bear in mind throughout that water analysis deals with material present in very minute quantity, and that the least carelessness in collecting the sample must vitiate the results. Note the date of taking the sample, record the temperatures of both air and water and give as full a description as possible of the soil through or over which the water flows, together with the immediate sources of possible contamination.

Sketch the surroundings of the place of collection and give approximate distances of houses, privies, barns, and fertilized land, noting the general character and topography of the local watershed; in other words, make a careful sanitary survey.

Having secured the sample, the analysis should be begun at once, for the reason that water is liable to rapid changes in character during storage. For instance, the following analyses are of the same sample of water from the laboratory tap, drawn November 10, and allowed to stand in the sampling bottle at ordinary room temperature:

TABLE 1

	Nov. 10	Nov. 12	Nov. 13	Nov. 14	Nov. 15	Dec. 15
Free ammonia. . . . .	0.037	0.042	0.042	0.050	0.075	0.060
Albuminoid ammonia. . .	.220	.178	.191	.175	.155	.205
Chloride. . . . .	4.5					
N in nitrites. . . . .	trace	trace	trace	trace	trace	none
N in nitrates. . . . .	.50	.525	.55	.60	.60	.60
Required oxygen. . . . .	4.35	4.6	4.2	4.4	4.1	4.6
Total solids. . . . .	140.					

This water shows gradual oxidation of the nitrogen contents to nitrates, but on the whole is fairly stable. As showing, on the other hand, how rapid and how irregular the storage changes may at times be, the following analyses by Liversidge are given.<sup>1</sup>

<sup>1</sup> Chem. News, lxxi, 249.

These are, of course, exaggerated cases containing high ammonias, but they serve to point out the necessity of avoiding delay between the collection of the sample and the beginning of the analysis.

TABLE 2

	Horse Pond		Fish Pond		Peaty Water	
	Free ammonia	Albu-minoid ammonia	Free ammonia	Albu-minoid ammonia	Free ammonia	Albu-minoid ammonia
December 11	10.00	7.00	0.12	0.90	0.72	0.19
12	2.00	2.00	.11	.92	1.12	.04
13	8.00	4.00	.16	1.04	1.12	.13
15	7.00	4.00	.16	1.03	1.08	.12
16	6.00	2.00	.38	.69	.03	.04
19	5.00	2.00	.52	.56	.02	.03
20	4.00	1.00	.70	.38	.01	.01
21	2.00	.50	.90	.30		
January 8	.50	.25	1.38	.06		
10	.07	.07	1.50	.04		

Determination of dissolved gases should be done in the field.

Not long since no small confusion existed on account of the many ways in which the results of water analyses were stated, but this difficulty is now nearly done away with by the more general acceptance of the recommendation that all results be given in *parts per million in weight*. This method has the advantage that a liter, or fraction thereof, of water having been operated upon, and the substances found having been determined in milligrams, no long arithmetical calculations are required.

Of course the assumption is made that a liter of water weighs a kilogram—a true enough statement for potable

waters, but one capable of introducing error when mineral waters are dealt with whose specific gravities are appreciably above unity. In such a case the water to be analyzed is actually weighed, or else its weight is estimated from the known specific gravity and volume.

It is not usual to take these precautions unless the error introduced by omitting them approaches the allowable analytical error which is ordinarily set at .2 to .3 per cent of the substance determined. Twenty-five degrees centigrade and 6500 p.p.m. are the limits for temperature and total solids, respectively. A liter of pure water at 25° C. weighs 997 grams and a liter of brine containing 6573 milligrams of NaCl weighs 1003 grams at 20° C. The neglect of temperature in the first case or concentration in the second case introduces an error of .3 per cent.

Water should not be filtered before analysis unless so specified. If sediment be present, it should be equally distributed by thorough shaking before measuring.

The reason for this is that a water analysis should represent the water as the consumer uses it, and not in a condition improved by filtration.

Water analysis cannot be conducted in a general laboratory, because many of the tests would be ruined by the fumes common to such a locality.

#### TURBIDITY

Turbidity was formerly reported in words, not figures. In order to express it in parts per million, the writer some years ago suggested the use of a standard suspension made by adding one gram of exceedingly fine kaolin (obtained by elutriation) to one liter of distilled water. Each cubic centimeter of this preparation will contain one milligram of suspended clay.

Whipple and Jackson improved this standard by substituting fine diatomaceous earth for the kaolin, and later the United States Geological Survey introduced the use

of Pear's precipitated fuller's earth, in which form it is used to-day. The earth is ignited, ground, passed through a 200-mesh sieve and weighed. One gram being suspended in one liter of water gives a turbidity of 1000. Suitable dilutions of this standard suspension are kept in bottles of the size used for water samples and a series of "turbidities" is thereby obtained ready for instant use. A few crystals of mercuric chloride are added to each bottle to prevent organic growths.

Such a stock solution as this, when diluted with nine times its volume of water, will permit of a platinum wire one millimeter in diameter being just visible at a depth of 100 millimeters below the water surface.

A turbidity rod, prepared for the United States Geological Survey and based upon this standard, is very convenient for use in the field.

The eye of the observer must be about 1.2 meters above the wire, and the reading should not be made in direct sunlight. The rod cannot be used for turbidities below seven. For turbidities over 500 the water should be diluted before the observation is made.<sup>2</sup>

It must be noted that high color interferes with the use of the turbidity rod. Thus the writer found that the water of the Black River at Georgetown, S. C., which showed a color of 162, gave a rod reading of 31, while its true turbidity was only five.

Any quickly subsiding material present should be classed as "sediment" rather than "turbidity." To determine this it would be best to decant the water from above such deposit and then catch it upon a weighed filter or in a Gooch crucible.

When the turbidity is very high, as it is in some rivers, it often varies markedly in settleability as well as in amount. Some operators of filter plants handling water of such a variable character have adopted the practice of determining the turbidity of the raw water both imme-

<sup>2</sup> Circular 8, Div. of Hydrography.

diately and after an hour's quiescent settling. The variations observed are very interesting. For example, take two samples of raw water on separate days which show the same original turbidity, the first may show a decrease in turbidity of 25 per cent on an hour's settling, while the second may show a decrease of 75 per cent in the same time. The results of such a test are very useful in controlling the dosage of coagulant.

Some operators have found a very sensitive turbidimeter based on the principle of the Tyndall cone (see any text on colloid chemistry) useful, especially in research work (J. Ind. Eng. Ch., 18, 311). The use of the "candle" type turbidimeter is sometimes preferred for measuring high turbidities. In this form the water is poured into a calibrated tube until the image of some illuminated object (candle flame) placed beneath the tube just disappears. The calibrations on the tube give the turbidity direct (see manufacturer's literature).

"Suspended," as distinguished from "dissolved," material may be determined by estimating the solids (see page 110), both before and after passing the water through a Gooch crucible or a Berkefeld filter.

## ODOR AND TASTE

There are really only four different taste sensations—sour, sweet, salt, and bitter. All other seeming sensations of taste are actually produced by odors.

An exact and reproducible estimation of the quality and quantity of the odor and taste of a water is a rather difficult determination to make. And exactness in this determination is probably of little importance.

A record of the presence or absence of a detectable taste at room temperature and a detectable odor at room temperature and when hot will serve most cases. An estimation of the intensity of the odor may be made, if



desired. The following list<sup>3</sup> of odors (together with abbreviations) commonly found in waters will aid in completing the record:

a—aromatic	m—moldy
C—free chlorine	M—musty
d—disagreeable	p—peaty
e—earthy	s—sweetish
f—fishy	S—hydrogen sulphide
g—grassy	v—vegetable

### TEMPERATURE

A cool water, if possible, should be supplied for public use, but studies of temperature are comparatively rare, for the sufficient reason that questions of much greater weight determine the selection of a source of supply. The item of temperature is, however, well worthy of consideration. No small economy in the matter of the ice bill will follow the introduction of a cold water in place of one equally pure but warmer.

The advantage is especially noticeable in the poorer sections of the city.

For comparison: in June, 1906, with the atmospheric temperature at 76° F., the water of Troy, N. Y., as delivered to the consumer, was 66°, and required further chilling to make it acceptable to the taste. At the same time the deep-well supply of Ithaca, N. Y., stood at 56° and was agreeable for drinking without more cooling.

The extreme variation of temperature for Croton water, as delivered by the street hydrants in New York City, for the year 1894, was:

On February 24 ..... 34° F.

On August 4 ..... 76° F.

<sup>3</sup> Whipple, G. C., The Observation of Odor as an Essential Part of Water Analysis: Pub. Health Papers and Repts., Am. Pub. Health Assoc., 25, 587-93 (1899).

Should many temperature readings in deep water, as in a lake, be decided upon, no better device could be chosen for the work than the "thermophone," invented by Warren and Whipple. The following is clipped from a description issued by the makers, E. S. Ritchie & Sons, Brookline, Mass.:

The thermophone is an electrical thermometer of the resistance type. It is based upon the principle that the resistance of an electrical conductor changes with its temperature, and that the rate of change is different for different metals.

The operation of taking a reading is as follows: Having connected the leading wires to the proper binding posts of the indicator box, the current is turned on and the telephone held to the ear. A buzzing sound in the telephone is found to increase or diminish according as the pointer is made to approach or recede from a certain section of the dial. By moving it back and forth a position may be found where the telephone is silent. When at this point the hand indicates the temperature of the distant coil. Instruments of ordinary atmospheric range, i.e., from  $15^{\circ}$  to  $115^{\circ}$  F., may easily be read to  $.1^{\circ}$  even by an inexperienced observer. With a smaller range, or with an instrument having a larger dial, a greater precision may be obtained.

It is more sensitive than a mercurial or other expansion thermometer, because the rate of change of resistance per degree is greater than the rate of expansion of liquids or solids, and, moreover, slight changes in resistance may be more easily and accurately measured than slight changes in length or volume.

It sets quicker than most mercurial thermometers. In obtaining the temperature of water of various depths one minute has been found to be sufficient time to allow for setting.

## REACTION

The reaction of natural water is commonly slightly alkaline, although waters holding much free acid in solution, usually sulphuric, are by no means rare.

**Determination of Alkalinity.**—Place 100 c.c. of the water in a casserole and titrate with N/50 sulphuric acid,

using two or three drops of methyl orange (.5 gram in one liter of distilled water) as an indicator. Should the water be originally acid, make it slightly alkaline with a known amount of standard potassium hydroxide before titration. It is convenient to report alkalinity as representing so many parts of  $\text{CaCO}_3$  per million of water, and to note that such a form of result is quickly obtained by multiplying the number of cubic centimeters of sulphuric acid, used in the above titration, by 10.

Acidity may be stated in the same terms, using a negative sign, or else as  $\text{H}_2\text{SO}_4$ .

Information is sometimes desired as to the cause of the alkalinity of a water. Is it due to hydroxides,<sup>4</sup> carbonates, or bicarbonates? To determine this point advantage is taken of the difference in action of two indicators toward these several compounds. Thus, while hydroxides, carbonates, and bicarbonates react "alkaline" with methyl orange, only the former two so react with phenolphthalein (5 grams in one liter of 50 per cent alcohol). While, therefore, the "alkalinity" determined by the use of methyl orange or erythrosine might represent that produced by any single one of the three classes of substances mentioned, or else by a mixture of carbonates and bicarbonates on the one hand or of carbonates and hydroxides on the other, the "alkalinity" as measured by phenolphthalein (using one cubic centimeter of the alcohol solution noted) could be due only to the hydroxides present plus one-half the normal carbonates.

The following conditions are possible:

1. If the alkalinity determined by the use of phenolphthalein (*P*) should be zero, then the alkalinity shown by methyl orange or erythrosine (*M*) would be due to bicarbonates alone.
2. If *P* should be equal to one-half *M*, then the alkalinity would be due to normal carbonates alone.

<sup>4</sup> As in the effluents from softening plants.

3. If  $P$  should be less than one-half  $M$ , then both carbonates and bicarbonates would be present and their quantities would be:

$$\begin{aligned}\text{Carbonates} &= 2P, \\ \text{Bicarbonates} &= M - 2P.\end{aligned}$$

4. If  $P$  should be greater than one-half  $M$ , then bicarbonates would be absent and the alkalinity would be due to carbonates and hydroxides, and their quantities would be:

$$\begin{aligned}\text{Carbonates} &= 2(M - P), \\ \text{Hydroxides} &= M - 2(M - P) = 2P - M.\end{aligned}$$

#### DETERMINATION OF THE HYDROGEN ION

Alkalinity and acidity, as defined and determined in the preceding section, are *capacity* factors and give measures of the total *amount* of acid or alkali present no matter whether the acid or alkali is "strong" or "weak." Two solutions containing equivalent amounts of NaOH and  $\text{Ca}(\text{HCO}_3)_2$ , respectively, would show the same titration value or "total alkalinity," yet the former would have a "bitter" taste while the latter would be tasteless or pleasant. Corrosion would be slow in the first solution, but relatively rapid in the second. To distinguish between these two solutions there is needed an *intensity* factor. The "strength" or intensity of an acid or base is determined by the degree to which it changes the hydrogen-ion concentration when dissolved in pure water.

From the mass law and the ionization theory we know that  $\text{H}^+ \text{ conc.} \times \text{OH}^- \text{ conc.} = \text{a constant} = 1 \times 10^{-14}$  (NTP) in any dilute aqueous solution. So we can express the strength of either an acid or a base in terms of either the  $\text{H}^+$  concentration or  $\text{OH}^-$  concentration of its solution. It happens that the  $\text{H}^+$  concentration has been chosen for this purpose. A "strong" base then is a substance which greatly decreases the  $\text{H}^+$  concentration of water and a "strong" acid greatly increases it. Pure

water has an  $H^+$  concentration of  $1 \times 10^{-7}$  moles per liter, a normal acid  $1 \times 10^0$  and a normal alkali  $1 \times 10^{-14}$ . Most natural waters range between  $1 \times 10^{-6}$  and  $1 \times 10^{-8}$  moles per liter  $H^+$  concentration. Since these figures are cumbersome it has become customary to express these values in terms of the log of  $\frac{1}{H^+ \text{ conc.}}$ . These values become then 7, 1, 14, 6 and 8, respectively. Purely as a

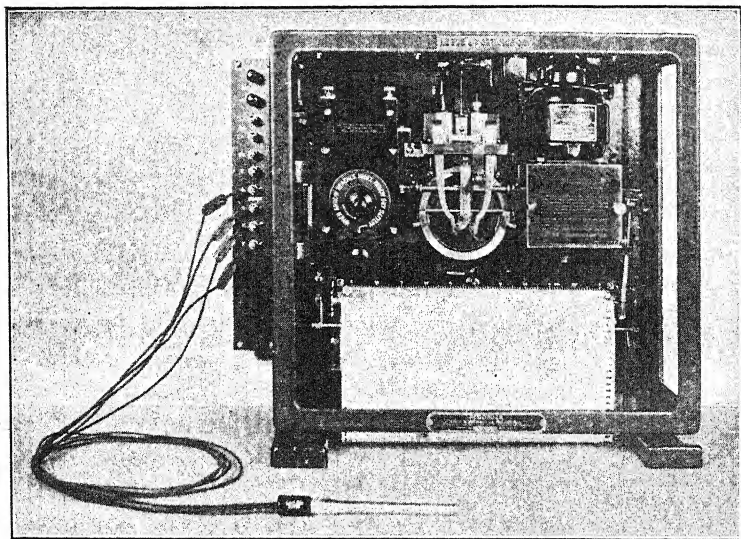


FIG. 1.—Potentiometer Recorder.

matter of chance such values have come to be called the " $pH$ ," or the " $pH$  value," of the solution. Since this terminology has become so generally accepted, we shall describe the determination of the intensity factor of alkalinity in such a manner that the results are obtained as  $pH$  values  $\left( pH = \log \frac{1}{H^+ \text{ conc.}} \right)$ .

The determination may be carried out with a hydrogen electrode (Figs. 1 and 2) whose voltage varies with the  $pH$ . Detailed directions for this method are furnished by the

manufacturers of the electrical equipment, or they will be found in any text on physical chemistry. The most convenient laboratory method depends upon the fact that

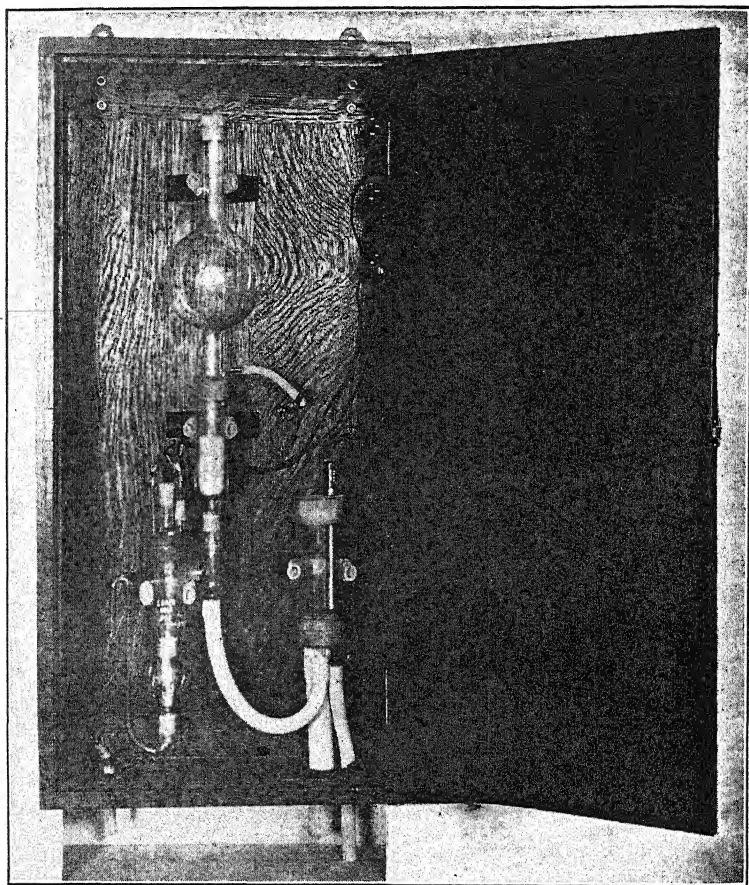


FIG. 2.—Continuous Type Quinhydrone Electrode.

many organic dyes change color progressively with the  $pH$  of the solution. This method requires a series of solutions of known  $pH$  and an appropriate set of indicators. The color produced when an indicator is added to the unknown is matched against the proper standard.

In routine laboratory work 25-c.c. test tubes are used for the unknown and the standards. If the standards are to be kept for any length of time tubes of insoluble glass should be used.

Ten cubic centimeters is the usual quantity of standard and unknown used for the test, and for this quantity 5 drops (.5 c.c.) of indicator of the strength specified later is the proper amount to use. The colors are matched by viewing the tubes horizontally against a white background. If the unknown is colored or turbid, a tube of the unknown without the dye should be placed behind the standard and a tube of distilled water placed behind the sample of unknown to which the indicator has been added, and the comparison made in such a manner as to compensate for the condition of the unknown.

For general use the indicators are dissolved with 1.1 equivalents of NaOH in sufficient water to give an .04 per cent solution. For class work brom cresol purple and phenol red are satisfactory indicators and cover a sufficiently wide range for most purposes.

The following are directions for the preparation of pH standards between 6.0 and 8.0 as given by Clark.<sup>5</sup>

**M/5 Acid Potassium Phosphate Solution.**—A high-grade commercial sample of the salt is recrystallized at least three times from distilled water and dried to constant weight at 110-115° C. A fifth molecular solution should contain 27.232 grams in one liter. The solution should be distinctly red with methyl red and distinctly blue with brom phenol blue.

**M/5 Sodium Hydroxid Solution.**—This solution is the most difficult to prepare, since it should be as free as possible from carbonate. A solution of sufficient purity for the present purposes may be prepared from a high-grade sample of the hydroxid in the following manner: Dissolve 100 grams NaOH in 100 c.c. distilled water in a Jena or pyrex glass Erlenmeyer flask. Cover the mouth of the flask with tin foil and allow the solution to stand overnight till the carbonate has settled. Then prepare a

<sup>5</sup> Clark, W. Mansfield, *The Determination of Hydrogen Ions*, pp. 194, 195-7, and 200: Williams and Wilkins, 1928.

filter as follows: Cut a "hardened" filter paper to fit a Buchner funnel. Treat it with warm, strong (1:1) NaOH solution. After a few minutes decant the sodium hydroxid and wash the paper, first with absolute alcohol, then with dilute alcohol, and finally with large quantities of distilled water. Place the paper on the Buchner funnel and apply gentle suction until the greater part of the water has evaporated, but do not dry so that the paper curls. Now pour the concentrated alkali upon the middle of the paper, spread it with a glass rod, making sure that the paper, under gentle suction, adheres well to the funnel, and draw the solution through with suction. The clear filtrate is now diluted quickly, after rough calculation, to a solution somewhat more concentrated than N/1. Withdraw 10 c.c. of this dilution and standardize roughly with an acid solution of known strength, or with a sample of acid potassium phthalate. From this approximate standardization calculate the amount required to furnish an M/5 solution. Make the required dilution with the least possible exposure, and pour the solution into a *paraffinned* (the author finds that thick coats of paraffin are more satisfactory than the thin coats sometimes recommended; thoroughly clean and *dry* the bottle, warm it and then pour in the melted paraffin. Roll gently to make an even coat and, just before solidification occurs, stand the bottle upright to allow excess paraffin to drain to the bottom and there form a very substantial layer) bottle to which a calibrated 50-c.c. burette and soda-lime guard tubes have been attached (see Fig. 33). The solution should now be most carefully standardized. One of the simplest methods of doing this, and one which should always be used in this instance, is the method of Dodge (1915), in which use is made of the acid potassium phthalate purified as already described. Weigh out accurately on a chemical balance with standardized weights several portions of the salt of about 1.6 gram each. Dissolve in about 20 c.c. distilled water and add 4 drops phenolphthalein. Pass a stream of CO<sub>2</sub>-free air through the solution and titrate with the alkali till a faint but distinct pink is developed. It is preferable to use a factor with the solution rather than attempt adjustment to an exact M/5 solution.

Very satisfactory standards and indicator solutions may now be purchased from reliable manufacturers, such



as La Motte Chemical Company. Unless an analyst is thoroughly trained in analytical and physical chemistry and has at his disposal a well-equipped laboratory he should not attempt the preparation of  $pH$  standards.

Most natural waters show a  $pH$  a little above 7.0, due to the presence of calcium carbonates. Swamp and mine waters may show a  $pH$  less than 6.0 and "alkali" waters or water from which the  $CO_2$  has been removed by photosynthesis may show a  $pH$  above 8.0. Alum coagulation lowers the  $pH$  and lime softening raises it.

### COLOR

Hazen's platinum-cobalt color standard (Am. Chem. J., xiv, 300) is prepared as follows: Dissolve 1.246 grams potassium platinic chloride (which amount contains 500 milligrams of platinum) and one gram cobalt chloride crystals in 100 c.c. strong  $HCl$  and dilute with distilled water to one liter. This solution has a color of 500.

By placing 1, 2, 3, 4, etc., c.c. of such solution in 50-c.c. Nessler tubes and diluting to the mark with distilled water, standard colors of 10, 20, 30, 40, etc., are obtained. A similar Nessler tube is filled with the water to be examined and comparison is directly made with the color standard.

A water possessing a color in excess of 70 should be diluted before reading the color, and then allowance for the amount of dilution should be made.

Turbid waters should be filtered through filter paper or a Berkefeld filter before reading the color.

The investigations of the Boston Water Board show that both iron and manganese often enter largely as a cause of color in water from the stagnant layer of a deep pond. In general, the color of a peaty surface water is mainly due to colloidal solution of organic material.<sup>6</sup>

<sup>6</sup> An excellent paper by Mrs. Ellen H. Richards, The Coloring Matter of Natural Waters, is published in J. Am. Chem. Soc., January, 1896. See also The Nature of Color in Water, J. N. E. Water Works Assoc., March, 1917.

## AS TO ANALYTICAL "STANDARDS"

The establishment of hard-and-fast "standards for interpretation of analytical results" is simply an impossibility. Results which would be considered satisfactory for one locality might be entirely inadmissible in another. Local standards are the proper ones by which to be guided, and it is to be regretted that local "normals" are not more frequently found on record.

For New York and New England the information is more full, as is instanced by the fine charts of "normal chloride" prepared for those states.<sup>7</sup>

Following the description of each analytical process to be given hereafter there will be found a paragraph headed "Compares," but the expression must not be permitted to mislead. The intention is simply to place before the reader sundry data and the opinions of various authorities, and absolutely disclaim any desire to set boundaries to the free use of the analyst's good judgment.

CHEMICAL COMPOSITION OF NATURAL WATERS<sup>8</sup>

Since practically all known substances are soluble to at least a slight extent in water, a wide variation in the chemical composition of natural waters is to be expected. Table 3 is a list of substances which have been observed in water.

TABLE 3

## SUBSTANCES OCCURRING IN WATER \*

## I. COMMON INGREDIENTS:

Acids: carbonic, sulphuric, hydrochloric, silicic, etc., usually in combination.

Aluminium: oxide and sulphate.

Calcium: carbonate, chloride, sulphate, phosphate.

Iron: carbonate, bicarbonate, oxide, sulphate.

Lithium: carbonate, bicarbonate, sulphate, chloride.

Magnesium: sulphate, carbonate, bicarbonate, chloride.

\* Crook, Mineral Waters of the United States: Lea Bros., 1899.

<sup>7</sup> Water Supply and Irrigation Paper, No. 144: U. S. Geol. Survey.

<sup>8</sup> Buswell, The Chemistry of Water and Sewage Treatment: A. C. S. Monograph Series, No. 38, pp. 69-78, 1928.

TABLE 3—*concluded*I. COMMON INGREDIENTS:—*continued*

Potassium: carbonate, bicarbonate, chloride, sulphate, and phosphate.  
 Silicon: usually as silica or silicon dioxide; occasionally as the bicarbonate.

Sodium: chloride, carbonate, bicarbonate, sulphate.

## II. RARER INGREDIENTS:

Acids: crenic and apocrenic, usually as crenates.

Ammonium: nitrate, chloride, crenate.

Antimony: as oxide and sulphate.

Arsenic: arsenate of sodium and potassium; arsenous acid.

Barium: as baryta or barium oxide and the sulphate.

Boron: as baborate of soda, or borax.

Bromine: as bromides of sodium, potassium, etc.

Cadmium: as sulphate (very rare).

Caesium: as sulphate (very rare).

Chlorine: as chlorides; rarely free.

Cobalt: very rare.

Copper: very rare.

Fluorine: as fluorides in two or three springs.

Iodine: as iodides of sodium and potassium.

Lead: very seldom seen.

Rubidium: very rare.

Strontium: very rare.

Zinc: very rare.

Besides the mentioned solids the following gases are commonly found in mineral springs:

Carbonic anhydride, or carbonic-acid gas.

Hydrogen sulphide, or sulphuretted hydrogen gas.

Oxygen.

Nitrogen.

Carbureted hydrogen (very rare).

With so large a variety of substances found in waters it is natural that several classifications should be proposed. These different systems have been discussed and compared by Crook,<sup>9</sup> Haywood<sup>10</sup> and Bartow.<sup>11</sup> Haywood's modification of Peale's classification seems to be the most useful and is therefore given in Table 4.

<sup>9</sup> Mineral Waters of the United States, 1899.

<sup>10</sup> U. S. Dept. Agric. Bur. Chem. Bull. No. 91.

<sup>11</sup> Ill. State Water Survey Bull. No. 4.

TABLE 4  
CLASSIFICATION OF CHEMICALS FOUND IN WATER \*

Class	Subclass	Groups	
		Thermal	Nonthermal
I. Alkaline.....	Carbonated or bicarbonated Borated Silicated	Sodic Lithic Potassic Calcic Magnesic	Nongaseous Carbondioxated
II. Alkaline-Saline....	Sulphated Muriated Nitrated	Ferruginous Aluminic Arsenic Bromic Iodic	Sulphuretted Azotized Carbureted Oxygenated
III. Saline.....	Sulphated Muriated Nitrated	Silicious Boric	
IV. Acid.....	Sulphated Muriated		

\* Haywood, U. S. Dept. Agric. Bur. Chem. Bull. 91.

The classification of Haywood and Peale given was designed primarily for use in distinguishing different types of saline waters and really has little significance when applied to waters of low mineral content. The concentrations of saline waters reach very high figures; perhaps the highest are those for the Dead Sea, which is said by Raich <sup>12</sup> to have a salt content of more than 22 per cent. These saline waters are of interest principally from a therapeutic standpoint and really require treatment in a separate volume.

Bartow points out that these classifications are all of limited value since they refer to the *kinds* with no reference

<sup>12</sup> Chem. Ztg. 31, 845.

to the *amounts* of constituents. Two waters which carried the same substance in solution would be classed the same although the one might contain 200 and the other 20,000 parts per million of total dissolved matter.

#### UNITS FOR REPORTING WATER ANALYSES

The standard unit in this country is one part per million (p.p.m.), which for most ordinary cases is the same as milligrams per liter within the limits of analytical error. Some laboratories report in grains per gallon (gr./gal.) as well as parts per million. Since there are 58,300 grains in a United States gallon the factor parts per million to grains per gallon is .0583. The imperial gallon contains 70,000 grains and is used to some extent as a unit in Great Britain. Occasionally an analysis reported in parts per hundred thousand is seen in this country (apparently it is standard in England). There is also the French degree for reporting hardness, which is parts per 100,000 of calcium carbonate or equivalents, and the German degree, which is parts per 100,000 of calcium oxide or its equivalents.

#### CLASSIFICATION OF WATERS ACCORDING TO AMOUNT OF DISSOLVED CONSTITUENTS

The characterization of a water as "hard" or "soft," or "saline" or "non-saline," is so much a question of what one is accustomed to that to attempt a general classification is hazardous.

Since in waters of low total solid residue the principal constituents found are those which produce hardness, it is not necessary to distinguish between hardness and total solids in the following classification:

Class	Total Solids
Soft . . . . .	Less than 100 p.p.m.
Moderately hard . . .	100-200 p.p.m.
Hard . . . . .	200-500 p.p.m.
Saline . . . . .	500 p.p.m. and over

Such arbitrary limits are bound to be subject to criticism. The limit of 100 p.p.m. for soft water is chosen because it is just about the point where the water softener salesman begins to have difficulty in demonstrating the advantages of this treatment. Up to 200 p.p.m. the hardness of the water is not seriously complained about. Above 200 p.p.m. the mineral constituents of the water are a serious drawback for both domestic and industrial use. Above 500 p.p.m. the water has a salty or brackish taste detectable by most people and a cathartic effect is usually observable by persons not accustomed to so highly mineralized a water. The writer has known of the use of water containing 2000 p.p.m. total residue as a public supply. The average hardness by States in the United States is given in Fig. 4.<sup>13</sup>

#### SUBSTANCES COMMONLY FOUND IN NATURAL WATERS

The substances more commonly met with in natural waters and those which must be considered in water treatment are shown in Fig. 3, originally prepared by the author for publication in *Water Works Practice*, by the American Water Works Association. It must be noted that this figure does not purport to be an analysis of an actual water, but merely a list of the substances commonly or occasionally found. Sulphuric acid could not exist with calcium carbonate nor would sodium carbonate occur in a water containing calcium sulphate.

The combinations of substances commonly found have been classified by Bartow as follows:

Class I includes those waters which contain more than enough sodium to unite with all of the nitrate, chloride and sulphate ions.

<sup>13</sup> Collins, W. D., *Water Supply Paper*, No. 496: U. S. Geol. Survey.

## EXAMPLES

Determinations made by Analysis	Parts per Million	Hypothetical Combinations	Parts per Million	Grains per Gallon
Iron (Fe).....	1.2	Potassium Nitrate (KNO <sub>3</sub> ).....	2.3	.13
Manganese (Mn)...	0.0	Potassium Chloride (KCl).....	6.1	.36
Silica (SiO <sub>2</sub> ).....	14.1	Sodium Chloride (NaCl).....	1.8	.11
Nonvolatile.....	1.8	Sodium Sulphate (Na <sub>2</sub> SO <sub>4</sub> ).....	1.7	.10
Alumina (Al <sub>2</sub> O <sub>3</sub> )...	0.0	Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> ).....	77.3	4.52
Calcium (Ca).....	66.9	Ammonium Carbonate ((NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> )..	14.3	.83
Magnesium (Mg)...	31.4	Magnesium Carbonate (MgCO <sub>3</sub> ).....	108.7	6.34
Ammonia (NH <sub>4</sub> )...	5.3	Calcium Carbonate (CaCO <sub>3</sub> ).....	167.0	9.75
Sodium (Na).....	34.8	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ).....	1.7	.10
Potassium (K).....	4.1	Silica (SiO <sub>2</sub> ).....	14.1	.82
Sulphate (SO <sub>4</sub> ).....	1.2	Nonvolatile.....	1.8	.11
Nitrate (NO <sub>3</sub> ).....	1.4			
Chloride (Cl).....	4.0	Total.....	396.8	23.17
Alkalinity:				
Phenolphthalein..	0.0			
Methyl Orange...	376.0			
Residue.....	380.0			

Determinations made by Analysis	Parts per Million	Hypothetical Combinations	Parts per Million	Grains per Gallon
Iron (Fe).....	1.0	Potassium Nitrate (KNO <sub>3</sub> ).....	49.0	2.86
Manganese (Mn)...	0.0	Potassium Chloride (KCl).....	127.9	7.47
Silica (SiO <sub>2</sub> ).....	15.2	Sodium Chloride (NaCl).....	2083.8	121.69
Nonvolatile.....	0.5	Sodium Sulphate (Na <sub>2</sub> SO <sub>4</sub> ).....	119.7	6.99
Alumina (Al <sub>2</sub> O <sub>3</sub> )...	1.8	Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> ).....	250.7	14.64
Calcium (Ca).....	29.3	Magnesium Carbonate (MgCO <sub>3</sub> ).....	54.8	3.20
Magnesium (Mg)...	15.8	Calcium Carbonate (CaCO <sub>3</sub> ).....	73.1	4.27
Ammonia (NH <sub>4</sub> )...	0.0	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ).....	1.4	0.08
Potassium (K).....	86.0	Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	1.8	0.10
Sodium (Na).....	967.2	Silica (SiO <sub>2</sub> ).....	15.2	0.89
Sulphate (SO <sub>4</sub> ).....	81.0	Nonvolatile.....	0.5	0.03
Nitrate (NO <sub>3</sub> ).....	30.1			
Chloride (Cl).....	1325.0	Total.....	2777.9	162.22
Alkalinity:				
Methyl Orange...	362.0			
Residue.....	2792.0			

These waters would therefore contain sodium carbonate and possibly the carbonates of magnesium, calcium and iron. The waters of this class will form a sludge or soft scale when used in boilers.

Class II includes those waters which have sufficient sodium to unite with all of the nitrate and chloride and

with part of the sulphate ions present. These waters contain the sulphate of magnesium and sometimes the sulphates of calcium, iron and aluminum. The waters

## SUBSTANCES IN NATURAL WATERS

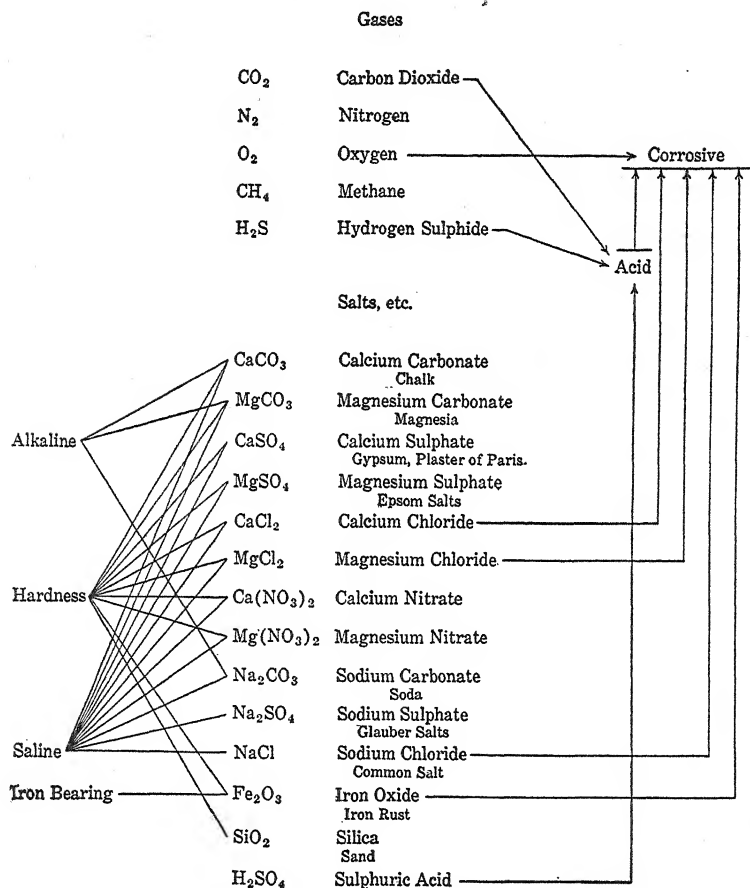


FIG. 3.

of this class will form a scale more or less hard, according to the proportion of sulphate present. Lime and soda are both required for softening.



## EXAMPLE

Determinations made by Analysis	Parts per Million	Hypothetical Combinations	Parts per Million	Grains per Gallon
Iron (Fe).....	0.8	Potassium Nitrate (KNO <sub>3</sub> ).....	2.8	.16
Manganese (Mn)...	0.0	Potassium Chloride (KCl).....	7.3	.43
Silica (SiO <sub>2</sub> ).....	8.9	Sodium Chloride (NaCl).....	19.0	1.11
Nonvolatile.....	3.6	Sodium Sulphate (Na <sub>2</sub> SO <sub>4</sub> ).....	27.8	1.62
Alumina (Al <sub>2</sub> O <sub>3</sub> )...	2.3	Ammonium Sulphate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )...	2.2	.13
Calcium (Ca).....	174.2	Magnesium Sulphate (MgSO <sub>4</sub> ).....	306.8	17.90
Magnesium (Mg)...	62.1	Calcium Sulphate (CaSO <sub>4</sub> ).....	37.4	2.18
Ammonia (NH <sub>4</sub> )...	0.6	Calcium Carbonate (CaCO <sub>3</sub> ).....	407.2	23.79
Sodium (Na).....	16.4	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ).....	1.1	.06
Potassium (K).....	4.9	Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	2.3	.13
Sulphate (SO <sub>4</sub> ).....	292.0	Silica (SiO <sub>2</sub> ).....	8.9	.52
Nitrate (NO <sub>3</sub> ).....	1.8	Nonvolatile.....	3.6	.21
Chloride (Cl).....	15.0			
Alkalinity:		Total.....	826.4	48.24
Methyl Orange...	394.0			
Residue.....	912.0			

Class III includes those waters in which the sodium is not present in sufficient quantity to unite with all of the nitrates and chlorides present. These waters will therefore contain magnesium chloride. The hardness may be due to chlorides, sulphates and carbonates of magnesium, calcium, etc. These waters will be corrosive and will form a hard scale when used in boilers.

The common notion that wells and springs maintain a constant chemical composition is apparently unfounded. Haywood<sup>14</sup> reports a decrease of 50 per cent in the mineral content of certain springs from 1871 to 1905, while the author has observed an increase of 100 per cent in the solids of certain wells in a period of twenty years.

<sup>14</sup> Loc. cit.

## EXAMPLES

Determinations made by Analysis	Parts per Million	Hypothetical Combinations	Parts per Million	Grains per Gallon
Iron (Fe).....	0.7	Potassium Chloride (KCl).....	27.6	1.61
Manganese (Mn)...	0.0	Sodium Chloride (NaCl).....	304.2	52.80
Silica (SiO <sub>2</sub> ).....	32.8	Ammonium Chloride (NH <sub>4</sub> Cl).....	6.9	0.40
Nonvolatile.....	8.0	Magnesium Chloride (MgCl <sub>2</sub> ).....	139.1	8.12
Alumina (Al <sub>2</sub> O <sub>3</sub> )....	2.6	Magnesium Sulphate (MgSO <sub>4</sub> ).....	141.6	8.27
Calcium (Ca).....	112.3	Calcium Sulphate (CaSO <sub>4</sub> ).....	180.6	10.55
Magnesium (Mg)....	64.2	Calcium Carbonate (CaCO <sub>3</sub> ).....	200.5	11.71
Ammonia (NH <sub>4</sub> )....	2.3	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ).....	1.0	0.06
Sodium (Na).....	355.8	Silica (SiO <sub>2</sub> ).....	32.8	1.91
Potassium (K).....	14.4	Nonvolatile.....	8.0	0.47
Sulphate (SO <sub>4</sub> ).....	189.7	Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	2.6	0.15
Nitrate (NO <sub>3</sub> ).....	0.0			
Chloride (Cl).....	670.0	Total.....	1644.9	96.05
Alkalinity:				
Methyl Orange...	250.0			
Residue.....	1660.0			

Determinations made by Analysis	Parts per Million	Hypothetical Combinations	Parts per Million	Grains per Gallon
Iron (Fe).....	1.4	Sodium Nitrate (NaNO <sub>3</sub> ).....	19.4	1.13
Silica (SiO <sub>2</sub> ).....	12.5	Sodium Chloride (NaCl).....	17.2	1.00
Nonvolatile.....	0.5	Ammonium Chloride (NH <sub>4</sub> Cl).....	0.9	.06
Alumina (Al <sub>2</sub> O <sub>3</sub> )....	0.9	Magnesium Chloride (MgCl <sub>2</sub> ).....	5.2	.31
Calcium (Ca).....	77.7	Magnesium Sulphate (MgSO <sub>4</sub> ).....	44.7	2.62
Magnesium (Mg)....	42.7	Magnesium Carbonate (MgCO <sub>3</sub> ).....	11.8	6.54
Ammonia (NH <sub>4</sub> )....	0.3	Calcium Carbonate (CaCO <sub>3</sub> ).....	194.0	11.35
Sodium (Na).....	12.0	Iron Oxide (FeO).....	2.0	.12
Potassium (K).....		Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	0.9	.05
Sulphate (SO <sub>4</sub> ).....	35.7	Silica (SiO <sub>2</sub> ).....	12.5	.73
Nitrate (NO <sub>3</sub> ).....	14.1	Nonvolatile.....	0.5	.03
Chloride (Cl).....	15.0			
Alkalinity:		Total.....	409.3	23.94
Methyl Orange...	318.0			
Residue.....	405.0			

**Mineral Waters.**—The mineral-water industry was originally confined to the bottling and sale of medicinal waters. With the advance of science some of the claims made for these waters were found to be unwarranted. It was found to be necessary to drink several hundred gallons of some so-called lithia waters in order to obtain a therapeutic dose.

With respect to radioactivity Skinner and Sale <sup>15</sup> state: "Of all waters, foreign and domestic, which have been analyzed, and from published data, it may be concluded that shippers are not justified in making statements on labels which would induce prospective consumers to purchase the waters because of their radioactivity. The largest radioactivity of a temporary nature was found in a water from a warm spring in Massachusetts. Permanent radioactivity was found in greatest measure in a deep well in Northern Ohio. To obtain a daily dose (2 micrograms) prescribed by the American Medical Association as a minimum, the patient would have to consume 2810 gallons of the warm spring water or 1957 gallons for the Ohio well."

The decline in production of medicinal waters has been largely offset by the production of table waters. Reviewing the mineral water industry from 1883 to 1923, Collins <sup>16</sup> reports that it rose from one million dollars in 1883 to eight and a half million in 1903, dropped to four and a half million in 1918, from which it had risen to six and a half million dollars in 1923. In 1923 the medicinal-water sales amounted to only 13 per cent of the total.

**pH of Natural Waters.**—Since most natural waters are buffered with calcium bicarbonate and carbonic acid we find their pH ranging from about 7.0 to 8.0. In soft waters the organic acids from vegetable decomposition may reduce the pH to 5.0 or even below, while photosynthetic action in relatively hard waters may raise it considerably above 8.0. The discharge of trade wastes, mine waters and so forth may produce conditions entirely abnormal.

**Composition of Rain Water.**—Considerable data on the composition of rain water have been obtained by various agricultural stations. Some data by Woehlk <sup>17</sup> show rather surprisingly large amounts of nitrogen and sulphur. The

<sup>15</sup> J. Ind. Eng. Chem. 14, 948 (1922).

<sup>16</sup> Mineral Resources of the United States: U. S. Geol. Survey, 1923, II, p. 109.

<sup>17</sup> Chem News, cxxvii, 3; Chem. Abstracts, xvii, 3558.

amounts of nitrogen compounds, chloride and sulphates in the rains and snows at Mount Vernon, Iowa, from Oct. 1, 1922, to June 1, 1923, were determined. The town has a population of 2500, without manufacturing enterprises, a condition which eliminates excessive smoke contamination of the atmosphere. Samples were collected in granite pans and every precaution was used to avoid contamination. In the period 70 inches of snow and 11.2 inches of rain fell, equivalent to 17.21 inches of rainfall. From analyses of samples of 12 snows and 29 rains it was calculated that 2.035 kg. of chlorine, .57 kg. of sulphur as  $\text{SO}_3$  and 3.93 kg. of nitrogen fell on each acre. In parts per million the chlorine varied from .345 to 2.81; nitrogen averaged .896 parts per million and was quite constant. Electrical storms seemed to be responsible for some of the higher amounts. The average parts per million of free ammonia were .34, albuminoid ammonia .264, nitrogen in nitrates was .346, in nitrites .397 p.p.m., and sulphur as  $\text{SO}_3$  .147 p.p.m. The amount of precipitation determines largely the number of pounds of nitrogen supplied per acre, although slight rains have a higher concentration of nitrogen than long rains. Determinations were made on the basis that one acre-inch of rain weighs 226,875 pounds.

#### TOTAL SOLIDS

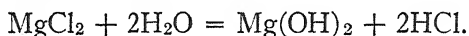
**Source.**—Material dissolved or suspended in water is naturally derived from the strata through which the water passes, or the surface over which it flows. Thus are obtained waters of all degrees of hardness and of a great variety of color and turbidity.

**Determination.**—Thoroughly shake the vessel containing the sample and then measure out 100 c.c. of the unfiltered water by means of a pipette into a weighed platinum dish.

Evaporate to dryness on the water bath, being careful to place a filter paper between the dish and the water in the bath in order to prevent any deposit of impurities on the under side of the dish. (A better plan is to make use of a porcelain

water bath filled with distilled water.) When dry, place the dish and contents in an air bath and maintain the temperature at 105° C. for half an hour. Cool in a desiccator and weigh. Replace in the air bath and repeat the weighing at intervals of half an hour until a constant weight be obtained. The final weight, less the known weight of the dish, will give the amount of total solids. This weight multiplied by 10 will give the weight of solids per liter of water, which, expressed in milligrams, will represent parts per million.

Should much  $\text{MgCl}_2$  be in the water, add a known amount of  $\text{Na}_2\text{CO}_3$  before evaporation, and allow for such addition in the final weighing. Otherwise there will be loss due to the decomposition of the  $\text{MgCl}_2$ .



The "*loss on ignition*" is obtained by gradually raising the dish and its contents to redness and reweighing after cooling in a desiccator.

It is important to note that while no quantitative results of much value are to be expected from the ignition in question, yet considerable insight may often be obtained as to the character of the water by observing the intensity of the charring and the presence or absence of fumes.

As Dr. Smart says: "The blackening during the process is of more interest than the mere loss of weight. No matter how few parts are lost, if the lining of the capsule blackens all over and the carbon is afterward dissipated with difficulty, the water is to be viewed as suspicious. What are called 'peaty' waters here constitute the exception."<sup>18</sup>

Angus Smith pointed out that "in water containing nitrates and nitrites no organic matter would be apparent on burning unless more should be present than these salts could oxidize"—a fact always to be borne in mind.

If it be desirable to distinguish between "suspended" and "dissolved" solids, the latter may be determined by

<sup>18</sup> Report Nat. Board of Health, 1880.

evaporating the water after passing through paper or a Berkefeld filter, and by subtracting such value from the "total solids" a knowledge of the amount of "suspended solids" is secured.

## COMPARATES\*

	P.p.m.
Average in sundry surface waters known to be pure.....	74
Average in sundry surface waters known to be polluted.....	194
Average in sundry ground waters known to be pure.....	144
Average in sundry ground waters known to be polluted.....	642

\* See page 21.

These averages are really of but small sanitary value, for the reason that a polluted water may be low in total solids, or *vice versa*, according to the character of the soil through or over which the water flows.

The Rivers Pollution Commission of Great Britain gives as averages out of 589 samples of unpolluted waters analyzed for total solids:

	P.p.m.
Rain.....	29.5
Upland surface.....	96.7
Deep well.....	432.8
Spring.....	282.

Colby considers <sup>19</sup> that water containing over 306 p.p.m. of carbonate of sodium or of common salt is not suitable for irrigation. He believes also that for drinking purposes the soluble salts should aggregate not over 680.

## HARDNESS

Before entering into the question of quantitative estimation, let it be premised here that "hardness" may be classified under two heads, viz., "noncarbonate" and "carbonate," and many samples of water possess them both. The former is occasioned by the presence of calcium sulphate and other soluble salts of calcium and magnesium held in

<sup>19</sup> Col. Agric. Expr. Sta., 1903.

solution by the solvent action of the water itself; such a water cannot be materially softened by boiling under ordinary pressure.

"Carbonate" hardness is caused by carbonates of calcium and magnesium held in solution as the bicarbonates by union with carbonic acid present in the water. Boiling such a water breaks up the union and expels the carbonic acid, whereupon the bulk of the calcium carbonate separates from solution. Magnesium carbonate, however, is soluble to the extent of 100 p.p.m.

It may be considered, in short, that the calcium or magnesium is present as a soluble bicarbonate which breaks upon boiling into water, carbonic-acid gas and the normal carbonate in which form the calcium precipitates. In this connection, A. H. Allen holds that it is not necessary to assume the existence of calcium bicarbonate. One water which he examined evolved very small quantities of carbon dioxide on boiling, and yet the precipitated calcium carbonate was large in amount. He considers it "probable that calcium carbonate is capable of existing in a soluble colloid condition, changing, on boiling the liquid, to the ordinary insoluble modification."<sup>20</sup>

"Noncarbonate hardness" is determined by Hehner's method.<sup>21</sup> The measured water is boiled to dryness with a known excess of  $\text{Na}_2\text{CO}_3$ . Recently boiled distilled water is added. Precipitated  $\text{CaCO}_3$  is filtered off, and the  $\text{Na}_2\text{CO}_3$  remaining in the filtrate is determined by titration with standard acid, using methyl orange or erythrosine as an indicator. The loss in  $\text{Na}_2\text{CO}_3$  is calculated to a corresponding amount of  $\text{CaSO}_4$ .

"Carbonate hardness" is often equal to the "alkalinity," previously determined (see page 13).

The latter may be the larger of the two, however, as, for instance, in the case of the presence of sodium or potassium carbonates or bicarbonates.

<sup>20</sup> J. Soc. Chem. Ind., vii, 801.

<sup>21</sup> Analyst, viii, 77.

The determination of carbonate hardness is necessary when analyzing a water for the purpose of calculating the chemicals necessary for softening by the lime-soda process. It also indicates whether the water will form a soft or a hard scale.

So far as action on soap is concerned the "total hardness" is the item of importance.

"Total hardness" is most satisfactorily determined by the usual quantitative methods for estimating calcium and magnesium.

#### ECONOMIC DISADVANTAGES OF UNSUITABLE WATERS<sup>22</sup> SOAP WASTE

Many of the substances contained in natural waters have chemical properties which are unfavorable to industrial and domestic use of the water. Most of these unfavorable properties are popularly referred to as "hardness." The term as sometimes used is rather indefinite. It is defined in Standard Methods of Water Analysis (American Public Health Association, 1923) as follows:

"Water which requires an excessive amount of soap to form a lather or forms much incrustation on vessels in which it stands or is heated is commonly called 'hard water.' Calcium and magnesium, and iron and aluminium to a less extent, are responsible for these effects. (The pseudohardness of brines is caused by their high sodium content which prevents solution of soda soaps.)"

The effect of hard water and the means for water softening appear to have been first discussed by a British chemist by the name of Th. Clark, who patented the lime process in 1841.<sup>23</sup> He later published several papers on the subject of softening by the use of lime and the use of soap solution to

<sup>22</sup> Buswell, The Chemistry of Water and Sewage Treatment: A. C. S. Monograph Series, No. 38, pp. 79-82, 1928.

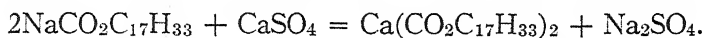
<sup>23</sup> Repertory of Patent Inventions for 1841. (Great Britain.)





determine the hardness of water. They are: A New Process for Purifying the Water Supplied to the Metropolis, by Th. Clark, London, 1849; On the Examination of Water for Towns for Its Hardness, by Th. Clark, Chem. Gaz. 5, 100 (1847), reviewed in detail by J. Moser, Wien Acad. Ber. 1850, April, p. 484; abstract Jahresbericht 3, 608.

**Soap Waste.**—The precipitation of soap by calcium and magnesium salts is probably one of the most commonly recognized disadvantages of hard water. The reaction is frequently written (assuming soap to be sodium oleate):



On the basis of this equation it should require about .05 pound of soap to neutralize a hardness of one part per million in 1000 gallons of water. The data reported in the literature based on experimental determination of soap wasted do not agree with this figure nor is there agreement among the different authorities. The various figures are given in Table 5.

From these data it appears that the reaction does not follow exactly the equation given. Evidently the precipitated lime soap adsorbs a variable amount of sodium soap, the amount decreasing as the hardness increases so that with waters of 200 p.p.m. or more the soap destroyed above that calculated from the equation is approximately 25 per cent.

Variations in the composition of soap and of the water used in the experiments would account in part for the variations from the equation. The figure .1 pound soap wasted per p.p.m. hardness per 1000 gallons of water appears to agree with laundry experience.

**Financial Loss Due to Soap Waste.**—A number of interesting figures have been given to emphasize the economic importance of soap waste due to hard water. Such calculations when applied to cities must be based on assumptions as to the amount of water used for washing with soap and the completeness with which the soap reacts with the lime salts, and must be considered as approximations. One

gallon per capita per day is usually taken as the amount of water used for washing. On this basis it was reported <sup>24</sup> that the removal of 72 p.p.m. of hardness from the water of the city of St. Louis resulted in a saving of \$920 worth of soap per day. The author has estimated that in a town of 40,000 inhabitants, using a water of 300 p.p.m. hardness, a

TABLE 5  
SOAP WASTE CAUSED BY HARDNESS OF WATER

Hardness in P.P.M.	Soap Wastes, Pounds per Thousand Gallons	Authority
63	0.03	Laundry Owners Nat. Assoc. Manual, 1924. Calculated from equation. Booth, Water Softening and Treatment. Several water-softener manufacturers, also Christie, Water, Its Purification and Use in the Industries, p. 14.
Any	.05	
Any	.093	
Any	.100	
76.5	.70	Robins, Macmillan and Bosart, Ind. and Eng. Chem. 18, 27 (1926).
153	.070	
236	.073	
25	.164	Whipple, The Value of Pure Water.
80	.209	
200	.192	
10	.160	Buswell and McRoberts, paper before American Chemical Society, Sept., 1924.
100	.071	
200	.065	
300	.063	

ton of soap is wasted per day. It is generally conceded that the saving in soap alone is greater than the cost of municipal water softening. The other benefits of soft water are clear gain. If this be true in the case of cities, where all of the water is softened, it is clear that for private installations and laundries, where it is practicable to limit the softening

<sup>24</sup> Report of Water Commissioner of St. Louis, 1922.

to that portion of the supply in which it is needed, the saving will be very considerable.

The waste of soap is not the only objection to hard water in laundering. The lime soaps tend to stick to the fabric and are not easily rinsed off. This causes spots and stains on the laundered article.

### BOILER SCALE

At least an equally serious effect of hard water is the formation of scale by hard waters when heated. The exact determination of the loss due to scale in steam boilers is rendered difficult by the fact that the water-softening process removes turbidity and corrosive substances along with scale-forming materials, so that a comparison of operating costs with and without treatment frequently includes other benefits than prevention of scale alone.

The University of Illinois Engineering Experiment Station Bulletin No. 11 reports the following losses in fuel efficiency due to the presence of scale in boilers:

TABLE 6  
LOSS IN FUEL EFFICIENCY DUE TO BOILER SCALE

Character of Scale	Thickness, Inches	Composition	Loss of Efficiency, Per Cent
Hard .....	1/50	Mostly carbonate	9.4
Soft .....	1/23	Mostly carbonate	7.2
Hard .....	1/32	Mostly carbonate	8.5
Soft .....	1/25	Mostly carbonate	8.0
Hard .....	1/25	Mostly sulphate	9.3
Hard .....	1/20	Mostly sulphate	11.1
Soft .....	1/16	Mostly sulphate	10.8
Soft .....	1/16	Mostly carbonate	11.0
Soft .....	1/16	Mostly carbonate	12.4
Hard .....	1/16	Mostly carbonate	12.6
Soft .....	1/11	Mostly carbonate	15.0
Hard .....	1/8	Mostly sulphate	15.9

In summarizing various data, Parr<sup>25</sup> states that a conservative estimate would place the loss in fuel efficiency at 10 per cent for each  $\frac{1}{16}$  inch thickness of scale.

The data on the effect of scale on locomotive boilers are more extensive and accessible than those of stationary boilers because of the work of the American Railway Engineers' Association in collecting them. The report of the Water Service Committee of this association for 1925 gives the saving per locomotive per year due to softened water as averaging \$1000 for each 10 grains of hardness, or \$5.88 for each part per million of hardness. Savings in localities where the raw water is very bad have run as high as \$8000 per locomotive per year. In 1914 this committee estimated the loss at 7 cents per pound of scale-forming material entering the boiler. This figure was recently revised to 13 cents due to generally increased cost of materials and labor. The 1925 report indicates that the revised figure is too low.

In undertaking the estimation of soap-consuming power, or "soap hardness," advantage is taken of the reaction stated. A solution of soap of known strength is prepared, and is then added little by little to a given quantity of the water to be examined, until a permanent lather is formed, whereupon, from the known quantity of soap solution used, the amount of "hardness" present may be calculated.

This soap test, commonly known as Clark's, is not as accurate as the conventional methods for the determination of calcium and magnesium, the error sometimes amounting to 10 per cent. In the hands of an experienced analyst the error can be sufficiently reduced so that the soap test may be used for the routine control of water-softening plants and, in fact, it is extensively so used. Objections to the soap test have come largely from analysts who overestimated its accuracy and naturally were disappointed with their results.

**Standard Soap Solution.**—Make up 10 liters stock solution by shaking vigorously approximately 100 grams of pure powdered castile soap in one liter of 80 per cent grain alcohol.

<sup>25</sup> Fuel, Gas, Water and Lubricants, p. 176.

Let this solution stand at least overnight and decant. Titrate against the  $\text{CaCl}_2$  solution and dilute with 70 per cent grain alcohol until one cubic centimeter of the resulting solution is equivalent to one cubic centimeter of the standard calcium chloride solution, making due and recorded allowance for a lather factor from at least five determinations. The lather factor will vary from .5 to 1.4 c.c. with different soaps. Carbon dioxide free water should be used for lather factor determinations and standardization of the solution. One cubic centimeter of this solution after subtracting the lather factor is equivalent to one milligram of calcium carbonate.

**Calcium Chloride Solution.**—Carefully weigh out one gram of pure  $\text{CaCO}_3$ . Dissolve in a little  $\text{HCl}$ . Evaporate to dryness. Add a little distilled water and again evaporate to dryness to expel the excess of acid. Dissolve the residue in distilled water and dilute to one liter. Each cubic centimeter of this solution will contain an amount of calcium chloride equivalent to one milligram of  $\text{CaCO}_3$ .

**Standardizing the Soap Solution.**—Place 10 c.c. of the calcium chloride solution in an eight-ounce glass-stoppered bottle, make the volume up to 100 c.c. with recently boiled but cooled distilled water, and run in the prepared soap solution from a burette, little by little (shaking after each addition), until a lather be formed which persists for five minutes. Even when the amount of soap solution required is approximately known, never add more than half a cubic centimeter at once, and never fail to shake after such addition.<sup>26</sup>

Observation of the lather should be made with the bottle lying on its side.

Note the amount of soap solution used. Now repeat the experiment, using 100 c.c. of pure water only (no calcium chloride solution), and again note the amount of soap solution required. This second reading will give the amount of soap solution (not in considerable quantity) used up by the 100 c.c. pure water, and by subtracting it

<sup>26</sup> Chem. News, August, 1886.

from the reading obtained in the first instance knowledge will be reached of the quantity of soap required for the calcium salt alone. Estimate now the value of one cubic centimeter soap solution in terms of calcium carbonate and adjust to make the soap as nearly equal to the  $\text{CaCl}_2$  solution as possible.

8.2 c.c. soap solution are required for 10 c.c. calcium chloride solution + 90 c.c. water.

0.6 c.c. soap solution is required for 100 c.c. water.

Hence

7.6 c.c. soap solution are required for 10 mg.  $\text{CaCO}_3$ .

Hence

1 c.c. soap solution corresponds to 1.316 mg.  $\text{CaCO}_3$ .

Therefore 31.6 c.c. of dilute alcohol must be added for each 100 c.c. of soap solution to make 1 c.c. = 1.00 mg.  $\text{CaCO}_3$ . Add 10 per cent less than the calculated amount and repeat the standardization. Ignore an error of one per cent.

Always place the date of standardizing on the bottle, and restandardize frequently, as the soap solution is not permanent.

**Determination.**—Place 100 c.c. of the water in the eight-ounce bottle, run in the standard soap solution in the manner already stated, read off the amount required to produce the lather, multiply by the known value for one cubic centimeter soap solution, multiply this again by 10, and there will be obtained the “soap hardness” expressed as so many parts of  $\text{CaCO}_3$  per million of water.

It was formerly customary to report hardness in “degrees” rather than parts per million, but the difficulty of deciding which of the several systems of degrees was referred to provoked so much confusion that a change was made to the present simpler mode of expression.<sup>27</sup>

<sup>27</sup> In England the Clark scale is still in use. Each degree corresponds to one grain of  $\text{CaCO}_3$  per imperial gallon of water, i.e., one part in 70,000. Water below 6 degrees is considered soft. In France one degree corresponds to one part of  $\text{CaCO}_3$  per 100,000 parts of water; in Germany one degree corresponds to one part of  $\text{CaO}$  per 100,000.

Magnesium salts decompose soap rather slowly; therefore, do not conclude that the end point has been reached until after the lather has been observed to readily return upon shaking after a few minutes' waiting.

If the "hardness" due to salts of magnesium be required separately, shake the water up with a little solid ammonium oxalate, filter off the precipitated calcium oxalate on a dry filter, and determine the "hardness" in the filtrate.

The unit, grains per United States gallon of 58,335 grains of  $\text{CaCO}_3$ , is numerically nearly the same as the German degree.

When a water is so hard as to require a greater amount of soap solution for the 100 c.c. of the water than suffices to saponify 14 milligrams  $\text{CaCO}_3$ , better results are obtained by diluting the water with an equal bulk (or more, if necessary) of distilled water, inasmuch as too heavy a precipitate of the calcium stearate appears to interfere with the proper lathering. Of course the influence of the additional quantity of water must be allowed for.

For constant results the hardness of a water should be taken at a temperature of  $15^\circ \text{C}$ .<sup>28</sup>

**Comparates.**—The average hardness of good waters as given by the Rivers Pollution Commission of Great Britain stands:

Rain.....	3
Upland surface.....	54
Deep well.....	250
Spring.....	185

---

Wanklyn allows..... 575

Middleton thinks that from 40 to 70 p.p.m. of hardness will give the most satisfactory results generally, and that the limit of hardness for public supply should be placed at 350 p.p.m.<sup>29</sup>

<sup>28</sup> J. Am. Chem. Soc., 44, ii, 347.

<sup>29</sup> Water Supply, p. 17.



Pearmain and Moor<sup>30</sup> consider that "a greater hardness than 300 is undesirable from the hygienic standpoint."

They classify as follows:

	Per Million
Very soft. ....	30 to 50
Moderate. ....	50 " 100
Hard. ....	100 " 300
Very hard. ....	above 300

The rating of water as "hard" or "soft" is very often a matter of local preference.

Thus the author has encountered cases of complaint from people using a water of as low a hardness as 30 p.p.m.; and has heard others describe as of "good quality for boiler and laundry uses" a water which ran 66 in hardness. After wide inquiry among industrial water users the author has concluded to classify waters (in the Eastern states) as "soft" which do not exceed 50 in hardness; to call those "hard" which exceed 100; and to consider the intermediate values as a sort of neutral ground where local conditions and preferences shall govern.

### CHLORIDE

Water is never found free from chloride,<sup>3</sup> yet, notwithstanding its constant presence, there is hardly a factor in the sum total of water analysis toward which attention is more quickly turned, or regarding which there is closer scrutiny.

✓ In most instances a chloride is present in the form of common salt, washed from the air or soil, or added as one of the constituents of sewage. Salt itself is, of course, unobjectionable in the quantity usually present, but, it being so largely used in our food, there is always warrant for suspecting sewage contamination where the figures for chloride run high.

True it is that those figures are at times misleading, but they, like other data in water analysis, must be con-

<sup>30</sup> Water Analysis, p. 48.

FIG. 5.  
STATE BOARD OF HEALTH  
MAP OF THE  
STATE OF MASSACHUSETTS.  
SHOWING  
NORMAL CHLORINE.



sidered with judgment, and due weight be accorded the character of local surroundings.

If the district whence a water comes be naturally rich in salt, as in the case of Central New York, such fact must be borne in mind when formulating an opinion as to quality. Comparison should be made with a local water, of the same general character, known to be pure; and for that purpose state maps, such as those issued for New York and the New England states, are most valuable, and their construction is well worth the expenditure of public money.

The normal chloride maps for Massachusetts and Connecticut are here given as illustrations. More complete "isochlor charts" will be found in Water Supply and Irrigation, Paper No. 144, United States Geological Survey.

The influence of the sea upon the "normal chloride" of these states is made apparent by the charts.

Such influence is naturally marked in an insular country like England.

"Normal chloride" of a district is the amount of chlorine occurring in the unpolluted waters thereof. Ponds are the best waters to use for its determination. The "normal chloride" for deep-seated waters should be placed in a separate class.

Variation in the chloride contents of rain water always occurs inland, although not to the same degree as upon the coast. For instance, the mixed monthly rain and melted snow near Troy, N. Y., during 1896, contained the following amounts of chlorine as chloride:

	Per Million		Per Million
January.....	2.50	August.....	2.00
February.....	1.07	September.....	0.60
March.....	1.55	October.....	3.00
April.....	0.75	November.....	2.25
May.....	1.25	December.....	2.50
June.....	1.15		—
July.....	1.05	Mean.....	1.64

While not strictly city rain waters, the Troy samples were doubtless affected by the neighborhood of the city.

Although varying with the locality, yet the amount of common salt lifted from the ocean in spray and subsequently dropped upon the land in rain is always noteworthy. Professor Clark reports the Rothamsted, England, figures as 24 pounds per acre per annum.

Ground water is more directly influenced than rain water by the presence of human habitation. Thus the Massachusetts Board of Health (1890 [1], 680) found that twenty persons per square mile will add on the average 0.1 p.p.m. of chlorine as chloride to the water flowing from such district.

The determination of chloride in water is extremely simple. It depends upon the fact that if to a solution of a chloride which has been colored yellow by addition of a little potassium chromate a solution of silver nitrate be added, white silver chloride will be produced until the last trace of chloride be disposed of, whereupon red silver chromate will begin to appear.

The reagents required are:

**Standard Silver Nitrate Solution.**—Prepared by dissolving 2.40 grams of crystallized silver nitrate in one liter of water. Each cubic centimeter of such a solution is of a strength sufficient to precipitate one-half milligram of chloride. In common with all other reagents for water analysis, it should be kept in bottles having caps covering the stoppers, such as are used for volatile liquids. Check this solution against the *Standard Sodium Chloride Solution*, p. 56.

**Potassium Chromate, Indicator.**—Dissolve 2 grams of the pure salt in 100 c.c. of distilled water. Should the reagent not be perfectly free of chloride, add a little silver nitrate until red silver chromate begins to precipitate; let the precipitate settle and decant the liquid for use.

**Determination.**—Fifty cubic centimeters of the water to be examined are placed in a large Nessler tube, one



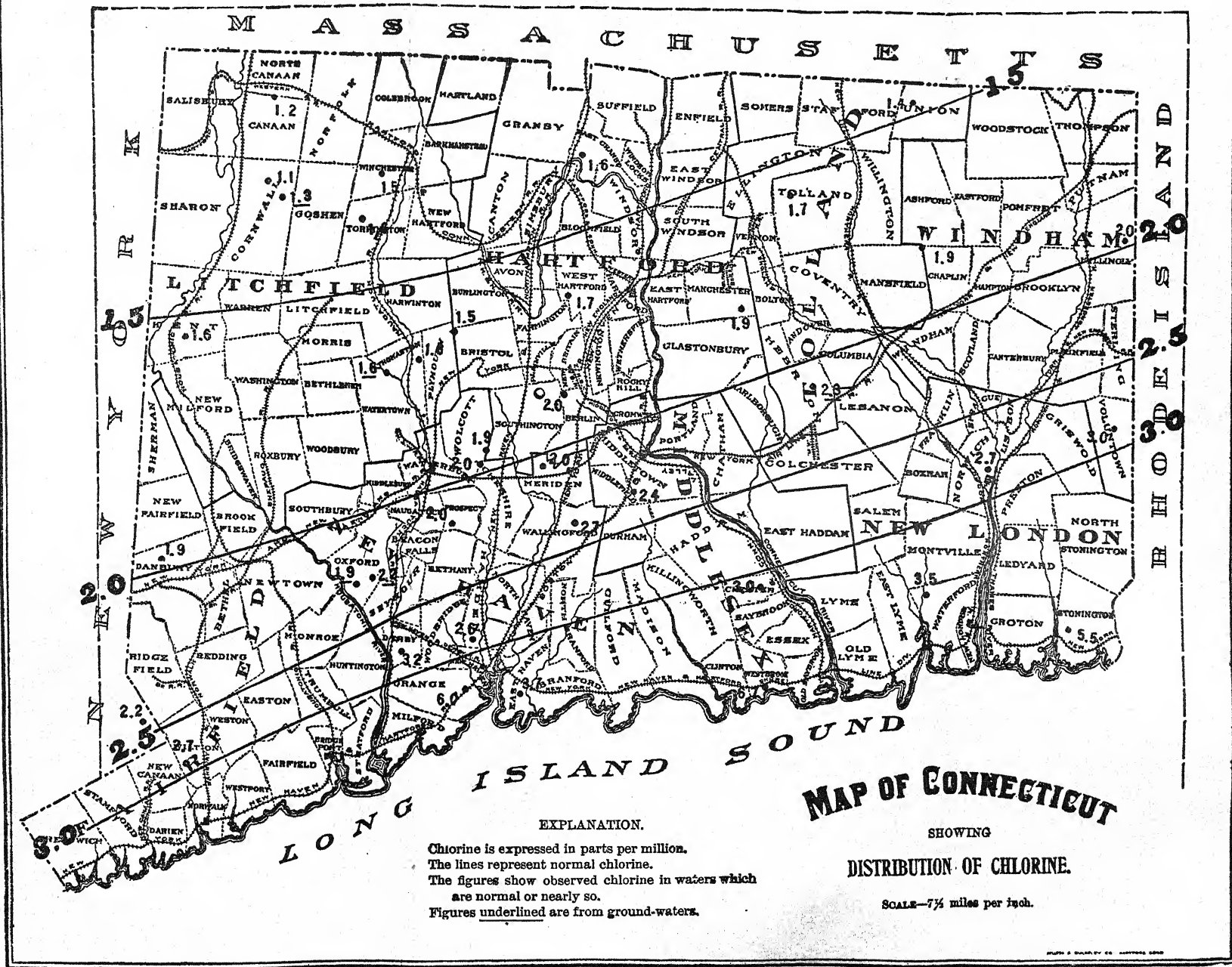
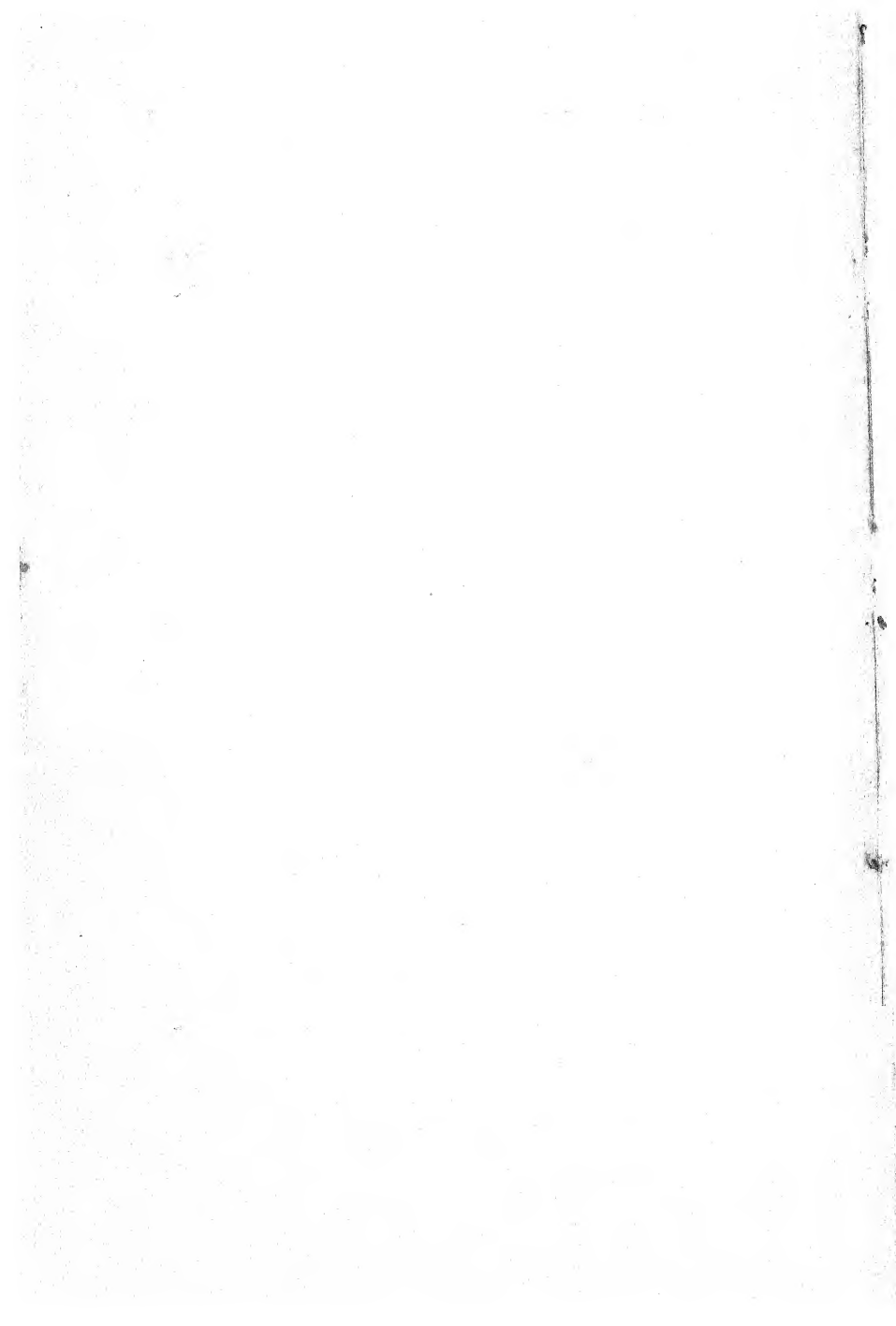


FIG. 6.



cubic centimeter of the potassium chromate solution is added, and mixed by the use of a glass plunger (see footnote, p. 52). The standard silver solution is then run in from a burette, until the red tint of the silver chromate just appears. Many analysts prefer a 6-inch porcelain evaporating dish for this determination, especially when speed rather than extreme accuracy is required. From the known amount of silver solution used the amount of chloride present is obtained, and this, multiplied by 10, will give the chloride in milligrams per liter or parts per million.

To determine with accuracy the first appearance of the red tint, it is best to make the examination in yellow light, either by the use of a photographic "dark room" lantern with a front of yellow glass, or by simply looking through a plate of such glass. Reflection from a porcelain tile throws the light through the length of the Nessler tube, and side light is cut off by a black screen. The author uses a box painted black on the inside and fitted with a top of yellow glass.

A second tube of the water, also colored with potassium chromate, should be provided in order that the formation of the red tint in the vessel operated upon may be, by comparison, more readily detected.

Acid waters should be neutralized with  $\text{Na}_2\text{CO}_3$  before beginning the chloride determination. On the other hand, should a water's alkalinity be due to normal carbonates or

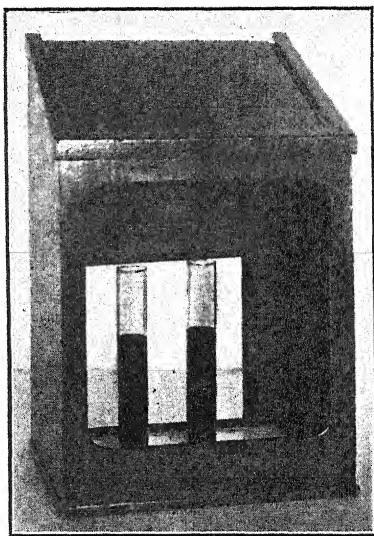


FIG. 7.—Camera for Chloride Determination.



to hydroxides, as in the case of an overdose of lime in the softening process, it should be neutralized with  $\text{H}_2\text{SO}_4$ , any excess of which is in turn neutralized with  $\text{Na}_2\text{CO}_3$ . In all of these cases the indicator used should be phenolphthalein.

Many waters possess such deep color, or such turbidity, as to interfere with proper titration; under such circumstances it is best to shake 500 c.c. of the water with 3 c.c. recently precipitated and washed aluminum hydroxide and then filter it, or allow it to stand twenty-four hours in a tall glass cylinder. The coloring matter or turbidity is thus removed, and the water cleared for use.

With waters high in chloride it is often very difficult to decide just when the red color begins to appear, for the reason that it is hard to compare the clear yellow liquid of the comparison vessel with one which has become turbid from precipitation of silver chloride.

In such a case it is well to roughly determine the chloride present and then to make a second determination, using for comparison 50 c.c. of the water to which has been added not only the chromate indicator, but also an amount of silver nitrate solution just short of that necessary to satisfy the chloride present.<sup>31</sup>

By these means the eye is greatly aided in noting the appearance of red tint, for in respect of turbidity both vessels are practically alike.

Should a sample smaller than 50 c.c. be taken because of the high chloride present the same must be diluted with distilled water to 50 c.c. before making the determination.

Circumstances sometimes demand, when the amount of chloride is very low, that a larger volume than 50 c.c. of the water be employed. For such purpose it is best to place the measured quantity of water in a porcelain casserole and to make it slightly alkaline with  $\text{Na}_2\text{CO}_3$  before concentration. After reduction of the volume to 50 c.c.

<sup>31</sup> For the analysis of brines Dr. S. L. Neave has worked out a special procedure: Determination of Chlorides in Salt Brine, Ind. Eng. Chem. Anal., Ed. 2, 1, 28 (1930).

the  $\text{Na}_2\text{CO}_3$  is neutralized with  $\text{H}_2\text{SO}_4$ , using phenolphthalein as an indicator, and the process is continued as already described.

It is important that the same volume (50 c.c.) be always secured before running in the silver nitrate solution; therefore, distilled water must be added if the concentration should have been carried too far.

The porcelain of the dish does not interfere with this determination, but it is very important to carefully scrub and wash down its sides after evaporation.

High chloride often causes confusion in reading the end point. After reading the burette a false end point must be always guarded against by the addition of several extra drops of the silver solution, which overdose will produce a marked red coloration if the true end point be already reached.

Although a water very high in chloride might be diluted before applying the method described, yet better results would be secured by employing

*Volhard's Process*, as follows: Take 100 c.c. of the water, or a larger bulk concentrated to that volume after addition of a little sodium carbonate. Add 3 or 4 c.c. ferric alum solution, and 2 c.c. strong nitric acid (free from nitrous fumes). Add *small*<sup>32</sup> excess of the standard silver nitrate solution. Filter, wash, and titrate the excess of silver with standard KCNS solution. The silver solution used up by the chlorine can be calculated. Do not omit to filter, as it avoids risk of action between the  $\text{AgCl}$  and  $\text{Fe}(\text{CNS})_3$ .

Saline mineral waters require gravimetric methods. About 400 p.p.m. of  $\text{NaCl}$  will produce taste.

#### COMPARATES<sup>33</sup>

	P.p.m.
Average in sundry surface waters known to be pure.....	3.57
Average in sundry surface waters known to be polluted.....	6.06
Average in sundry ground waters known to be pure.....	3.2
Average in sundry ground waters known to be polluted.....	91.7

<sup>32</sup> For objection to large excess, see *J. Am. Chem. Soc.*, xxxiii, 1344.

<sup>33</sup> See also p. 86.

The Rivers Pollution Commission reports the average amount of chlorine in 589 samples of unpolluted English waters as follows:

	P.p.m.
Rain.....	8.22
Upland surface.....	11.3
Deep well.....	51.1
Spring.....	24.9

(Great Britain being an island, chloride would naturally run high.)

Ordinary sewage, about 110 to 160.

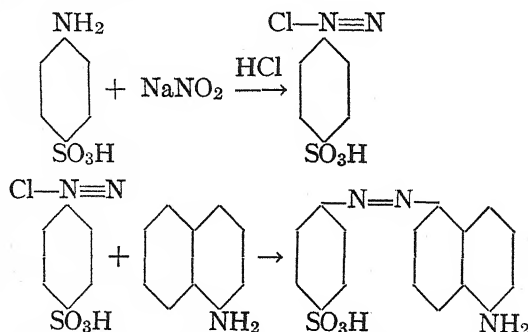
Human urine (average of 24 samples), 5872.

#### NITROGEN AS NITRITES

Broadly stated, the presence of nitrites, especially in shallow well water, is to be considered as unfavorable. They are at times due to a harmless reduction of nitrates, as by the iron piping of a well, but more commonly they are an *in transitu* product of the oxidation of the organic nitrogen derived from a source of contamination.

In either case it is necessary to estimate their quantity.

Of the several methods used of late for the determination of nitrites, the second one suggested by Griess seems to be the most deserving of favor. It depends in principle upon the red coloration ("azobenzol-naphthylamine sulphonic acid") produced whenever "sulphonic acid" and "naphthylamine hydrochloride" are added to an acidified solution of nitrite.<sup>34</sup>



<sup>34</sup> Richter's Organic Chemistry, 664, 665, 910.

The test is exceedingly delicate and is capable of distinguishing one part of nitrogen as nitrous acid in one thousand million parts of water.

The reagents required are prepared as follows:

**Sulphanilic Acid.**—Dissolve 8 grams of the salt in one liter of water containing 50 c.c. concentrated HCl.

**Naphthylamine Hydrochloride.**—Dissolve 5 grams of the salt in one liter of water containing 8 c.c. concentrated HCl.

**Standard Solution of Sodium Nitrite.**—Sodium nitrite may be bought, but its purity is always to be questioned, and, moreover, it is too deliquescent a salt to be weighed with ease and accuracy. It is better, therefore, to prepare the silver salt, which may be readily handled, and from it the solution required may be made.

**Basic Fuchsin.**—A solution of basic fuchsin containing .1 gm. per liter may be used for the preparation of permanent standards. Varying quantities are diluted with distilled water to match the desired standards. The exact quantities used are determined by trial.

**Standardization.**—To a cold solution of commercial sodium or potassium nitrite add a solution of silver nitrate as long as a precipitate appears. Decant the liquid and thoroughly wash the precipitate with cold water. Dissolve in boiling water. Concentrate and crystallize the silver nitrite from the hot solution. Dry in the dark at ordinary temperature (using vacuum is better) and keep it in a black bottle.

Weigh out .22 gram of the dry silver nitrite. Dissolve in hot water. Decompose with slight excess of sodium chloride, cool if necessary, and dilute to one liter. Allow the precipitated silver chloride to settle, remove 5 c.c. of the clear solution, and dilute the same to one liter. This second dilution (which is the standard solution to be used) will contain an amount of nitrite per cubic centimeter equivalent to .001 milligram of nitrogen.

**Determination.**—In order to undertake the determina-

tion of nitrites place 100 c.c. of the water to be examined (decolorized with aluminum hydroxide if necessary) in a Nessler tube. Add 2 c.c. of the sulphanilic acid solution, followed by 2 c.c. of the solution of hydrochloride of naphthylamine, mix,<sup>35</sup> cover with a watch glass, and set aside for ten to thirty minutes. Prepare at the same time other Nessler tubes containing known amounts of the standard solution of sodium nitrite and diluted to the 100-c.c. mark with nitrite-free distilled water, adding the reagents as above. At the end of the time stated (ten to thirty minutes) examine the depth of the pink color formed, and by comparing the unknown with the known an accurate determination of the amount of nitrogen present as nitrites may be made.

If much gas be burning in the room, nitrites will be in the atmosphere. Hence cover the tubes or remove them from the room during the half-hour interval before reading.

The error due to the presence of burning lamps is often much greater than is suspected.

**Comparates.**—In a report upon the presence of nitrites in eighteen "natural waters, believed from actual use to be of good, wholesome character," and collected from every variety of source, Mallet's determinations show an average of .0135 part nitrogen as nitrites per million parts of water. The average, by the same investigator, for nineteen waters "which there seems to be fair ground for believing have actually caused disease" is .0403 p.p.m.

The author's experience has been that the average amount of nitrites found in good waters is very much less than the value given by Mallet.

The absence of nitrites proves nothing. The author has had a most foul cistern water for analysis which showed but a trace of nitrites and no nitrates, and yet

<sup>35</sup> To accomplish this mixing it is best to use a stout glass rod ten inches long, at one end of which is fused a cross, composed of two pieces of glass rod  $\frac{1}{4}$  inch in length. The mixer is used as a plunger.

the water was contaminated with the entire house drainage and produced serious illness.

Average in sundry surface waters known to be pure.....	0.000
Average in sundry surface waters known to be polluted.....	0.006
Average in sundry ground waters known to be pure.....	0.000
Average in sundry ground waters known to be polluted.....	0.003

(See also page 77.)

### NITROGEN AS NITRATES

Nitrates present in water are but an additional step in the oxidation of nitrogenous organic matter.

They are more liable to indicate putrefaction of animal rather than of vegetable tissue, not only because of the greater quantity of nitrogen present in the former, but also on account of its more ready decomposition.

Stoddart claims that "natural waters can, at most, obtain but from  $\frac{1}{10}$  to  $\frac{2}{10}$  grain of nitrogen as nitrates per imperial gallon (1.43 to 2.86 per million) from sources other than animal matter; and practically the whole of the nitrogen of sewage may be oxidized into nitric acid without diminishing the risk involved in drinking it.

"The proposal to consider a water safe so soon as the nitrogen has assumed the oxidized condition, irrespective of the quantity that may be present, is entirely irrational."<sup>36</sup>

This warning is really unnecessary, for no one would risk an opinion based upon chemical data alone.

Results derived from a bacteriological examination, together with knowledge obtained from a sanitary survey, would supplement the chemical analysis and guard against an error of judgment.

Rain water washes a very considerable amount of nitric nitrogen from the atmosphere; thus an official report gives the following amounts of nitrogen as nitrates in sundry rain waters, showing at the same time the tendency of neighboring towns to increase this item:

<sup>36</sup> *Analyst*, xviii, 293.

	Parts per Million.
England, interior.....	0.19
“ cities.....	0.22
Scotland, near the coast.....	0.11
“ interior.....	0.08
“ cities.....	0.30
“ Glasgow.....	0.63
Montsouris, Paris, average of 18 years. ....	0.73

Nitrogen in the soil is increased by the fixing of atmospheric nitrogen through the agency of the roots of leguminous plants, such as peas, the process being aided by bacterial action.

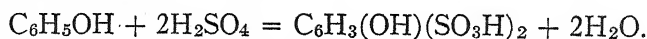
An interesting experiment to show this was recently made in France. Peas were grown in a closed space, and the nitrogen lost by the confined air was found equal to what was gained by the ground and plants. No such fixation of nitrogen was obtained when the soil was previously sterilized.

Such fixed nitrogen eventually enters the ground water, and a knowledge of the local “normal” for nitric nitrogen is consequently of advantage when studying the domestic well waters of a neighborhood.

Surface and shallow ground waters of good quality are low in nitrates, for the reason that such material is quickly absorbed by growing vegetation.

After having tried many ways for the determination of “nitrates” in potable water, the author has adopted a modification of the old so-called “picric acid method,” as giving, on the whole, the greatest satisfaction.<sup>37</sup>

Phenol disulphonic acid is made by the action of phenol on sulphuric acid:



This reagent, reacting with nitric acid, produces an intense yellow color upon addition of ammonium hydroxide.<sup>38</sup>

<sup>37</sup> The junior author after an extensive recent study of this determination has come to the same conclusion (J. Am. Water Works Association, 17, 388).

<sup>38</sup> *Analyst*, x, 200; also a discussion by Chamot, J. Am. Chem. Soc., xxxi, 922.

The intensity of this yellow color, produced in the water under examination, is compared with standard colors of known strength, and the quantity of nitrate present is thus determined.

The presence of high chlorides interferes with this process, resulting in readings decidedly lower than the truth. In such a case the addition of sodium chloride to the comparison standards will rectify the difficulty.

The "chloride" in the water under examination having been previously determined, an appropriate volume of standardized sodium chloride solution is added to each of the standard nitrate comparison solutions. Thus the water to be examined, and the nitrate solutions with which it is compared, all contain the same quantity of chloride. The results are satisfactory. If the chloride be below 30 p.p.m. it does not materially interfere with the nitrate determination.

The removal of chlorides, before testing for nitrates, may be accomplished by nearly neutralizing the alkalinity with  $\text{H}_2\text{SO}_4$  and then adding  $\text{Ag}_2\text{SO}_4$  solution (not to excess), filtering and using the filtrate to determine nitrates.

The solutions required for determination of nitrates are:

### Phenol Disulphonic Acid.

Sulphuric acid, pure and concentrated . . .	370 grams
Pure phenol . . . . .	30 "

Place these in a flask and keep the same surrounded by boiling water for six hours. Disulphonic, instead of monosulphonic acid, is thus produced by the prolonged high temperature, and reacts readily upon the nitrate.<sup>39</sup>

**Standard Potassium Nitrate Solution.**—Dissolve .7221 gram pure  $\text{KNO}_3$  in one liter distilled water. Evaporate 10 c.c. of this solution just to dryness on the water bath. Thoroughly moisten with 2 c.c. of the phenol disulphonic acid and dilute to one liter. Each cubic centimeter of

<sup>39</sup> Sanitary Investigation of the Illinois River, p. 9.



this solution will correspond to .001 milligram of nitric nitrogen.<sup>40</sup>

**Standard Sodium Chloride Solution.**—Dissolve 1.6485 grams pure fused NaCl in one liter distilled water. Each cubic centimeter will contain one milligram of chlorine.

**Standard Silver Sulphate Solution.**—Dissolve 4.4 grams  $\text{Ag}_2\text{SO}_4$  in one liter of distilled water. Each cubic centimeter of this solution corresponds to one milligram of chloride.

**Potassium Hydroxide Reagent.**—A solution about 12N (600 grams per liter) should be used.

**Determination.**—Take 100 c.c. (or less, according to nitrate contents) of the water that has been decolorized as per page 48. Remove chlorides with  $\text{Ag}_2\text{SO}_4$  if necessary and evaporate to dryness on the water bath. Thoroughly moisten the residue with 2 c.c. of the phenol sulphonic acid. Dilute with water and make alkaline with potassium hydroxide. Pour into a 100-c.c. Nessler tube. Dilute with water to the mark, mix and compare the depth of color with those produced by diluting different amounts of the standard potassium nitrate solution to 100 c.c., each such comparison tube having 2 c.c. potassium hydroxide reagent added before filling to the mark. The standards prepared as indicated are relatively stable and may be used for several weeks. The pure salt, tripotassium nitrophenoldisulphonate may be purchased for the preparation of nitrate standards. Solutions of this salt are even more stable if protected from light. In case the chloride be high there also should be added to each tube an amount of standard sodium chloride solution sufficient to correspond with the amount of chloride previously found to exist in the water, unless the chloride be removed by the  $\text{Ag}_2\text{SO}_4$  method.

The evaporations are best made in deep evaporating dishes of glass which easily hold 100 c.c. After dryness is reached, the dish, with its contents, should be at once removed from the water bath.

<sup>40</sup> *J. Infectious Diseases*, May, 1905.

The author prefers evaporating dishes of glass rather than porcelain for the reason that the residue to be treated is more easily seen.

In order to economize time, when dealing with waters low in chloride, it is convenient to make use of a series of standard "nitrate color solutions."

They keep their normal strengths of color quite well, but should not be trusted after having been a few weeks in stock.

Before evaporating for the nitrate determination it is best to remove turbidity and to decolorize the water with aluminum hydroxide as under *Chloride* (see p. 48).

#### COMPARATES <sup>41</sup>

Average in sundry surface waters known to be pure . . . . .	0.139
Average in sundry surface waters known to be polluted . . . . .	0.749
Average in sundry ground waters known to be pure . . . . .	1.4
Average in sundry ground waters known to be polluted . . . . .	11.9

The Rivers Pollution Commission gives the following averages from 589 unpolluted English waters for nitrogen as nitrites and nitrates *together*:

Rain . . . . .	0.03
Upland surface . . . . .	0.09
Deep well . . . . .	4.95
Spring . . . . .	3.83

As illustrating how widely the nitrates may vary in deep wells of good character the following list is taken from the *Analyst*, xx, 84:

Depth of Well in Feet	N as Nitrate
200. Stratford . . . . .	0.00
200. Wimbledon . . . . .	0.43
490. Chatham . . . . .	6.85
900. Southend . . . . .	0.71
600. Witham . . . . .	6.43
160. Mistley . . . . .	0.71
430. Braintree . . . . .	0.28
305. Colchester . . . . .	0.00
400. Norwich . . . . .	11.43

<sup>41</sup> See also p. 21.

It is frequently observed that deep waters have their nitrates entirely removed by the reducing action of the iron well casing. Under such circumstances the nitrogen appears as high "free ammonia."

Jamieson reports heavy nitrates in Connecticut well waters, and notes that they produce pitting in boilers. He found in a well water from the city of New Haven the nitrogen as nitrates as high as 41.3 p.p.m. He also gives a list of twenty other well waters running from 15.4 to 2 p.p.m.

Fresh sewage is usually found entirely free of either nitrites or nitrates simply because the organic nitrogen present has had, as yet, no sufficient opportunity to become changed to the oxidized form. For instance, a sample of the sewage of Troy, N. Y., contained:

	Parts per Million.		Parts per Million.
Free ammonia . . . . .	0.875	Chlorine . . . . .	31
Albuminoid ammonia. . .	0.675	"Required oxygen" . .	89
Nitrogen as nitrates . .	none	Total residue . . . . .	489
Nitrogen as nitrites . .	trace	Loss on ignition . . . .	315

A curious case of good water with very high "nitrates" came under the writer's observation. The water was from a deep rock-drilled well, which had been "torpedoed" by 50 pounds of nitroglycerine. Note how important the "history of the case" was to a proper interpretation of the analytical results in this instance.

#### NITROGENOUS ORGANIC MATTER

It will be remembered that the "cycle of organic nitrogen" may be represented as starting with the nitrogen firmly bound in the organic molecules, whence through the operation of disintegrating agencies that portion which does not gasify passes into the structure of other complex but less stable compounds until toward the end of its course it appears as a constituent, first of ammonia, then of nitrites, and finally of nitrates; after which, through the

availability of the last as plant food, it again starts upon its organic career.

It is desirable for us to trace if we can the progress of the nitrogen from its start in fresh and stable organic material to its finish in the mineralized nitrate form; and to measure its quantity in the successive steps of organic decomposition and inorganic oxidation.

The most general method now employed for obtaining information as to the nitrogenous organic matter is Wanklyn's

*Albuminoid Ammonia Process.* By the employment of this method a knowledge of the amount of "free ammonia" present is also obtained.

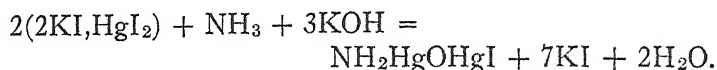
The process may be outlined as follows: The "free ammonia" is distilled from a measured quantity of the water, and its amount is determined by what is known as Nessler's method, which will be described later. A strongly alkaline solution of potassium permanganate is then added to another portion of the water and the distillation is repeated. Nitrogenous organic matters are thereby broken up and the resulting ammonia ("albuminoid"); which distills over with the "free," is determined by the Nessler method in like manner as before. It must be noted that the so-called "albuminoid" ammonia does not exist ready formed in the water, but is a product of the decomposition of organic nitrogenous substances by the alkaline permanganate. The term is derived from the fact that albumen gives off ammonia in like manner when similarly treated.

The reagents necessary are:

**Nessler's Reagent.**—Dissolve 35 grams potassium iodide (KI) in about 200 c.c. pure water. Add a saturated solution of mercuric chloride ( $\text{HgCl}_2$ ) until a faint show of excess is indicated. Add 160 grams solid potassium hydroxide (KOH). Dilute to one liter, and finally add a strong solution of mercuric chloride, little by little, until

the red mercuric iodide just begins to be permanent. Do not filter from excess of mercuric iodide, but let the same settle to the bottom of the vessel. The finished reagent should have a pale straw color. It is improved by age.

Nessler's reagent will give a distinct brownish yellow coloration with the most minute traces of ammonia or ammonium salts. If the quantity of ammonia be at all considerable, a brown precipitate will appear. The reaction in case of either precipitate or coloration will be



The author has had better results following this technique than with that described in "Standard Methods." The choice is largely a personal matter.

**Ammonia Free Water.**—This must be prepared with great care, in a room free from the usual laboratory fumes. In short, as has been already said, the entire examination of potable water should be undertaken in a locality other than a general working laboratory. A suitable retort for this purpose is of copper, five gallons in size, and with a tin condensing worm. Fill it with the best water obtainable, good spring water preferred, add a few crystals of potassium permanganate, distil, discarding distillate until about 20 to 25 per cent of the volume has distilled over, then collect distillate in 50-c.c. Nessler tubes, and to each successive tubeful so collected add 2 c.c. Nessler reagent.

No mixer or stirrer is ever employed in "Nesslerizing," as the high gravity of the Nessler reagent causes it to quickly sink into and mix with the comparatively light distillate. After waiting five minutes, should a brown tint be observed upon looking through the liquid (*longitudinally*) at a white porcelain tile or piece of white paper the presence of ammonia is indicated.

Continue the distillation and the Nesslerizing of the successive 50-c.c. portions of the distillate until no coloration is obtained after standing for five minutes. When

ammonia ceases to be detected, the distilled water may be collected for use. The distillation should not be pushed too far, both on account of danger to the retort and of possible production of ammonia from decomposition of the organic material remaining at the bottom.

**Alkaline Potassium Permanganate.**—Dissolve 200 grams solid potassium hydroxide KOH and 8 grams crystallized potassium permanganate  $\text{KMnO}_4$  in 1250 c.c. of pure water. Boil down in a porcelain dish to one liter and keep for use.

**Standard Ammonium Chloride Solution.** — Dissolve 3.819 grams of pure dry ammonium chloride in one liter of ammonia free water. Dilute 10 c.c. of this solution to one liter with ammonia free water. This second solution will represent a strength of .01 mg. of N per cubic centimeter, and is the standard solution used.

#### NITROGEN AS FREE AMMONIA

Fit a one-quart glass tubulated retort to a large Liebig condenser,<sup>42</sup> letting the neck of the retort pass well into the condensing tube. This connection must be thoroughly tight. Place 250 c.c. ammonia free water in the retort and add about  $\frac{1}{2}$  gram sodium carbonate. Distil off three 50-c.c. tubes of water, and Nesslerize the third in order to be sure that no ammonia yet remains in the retort. Any ammonia that may have resulted from the imperfect cleaning of the apparatus, or that may have been present in the sodium carbonate solution, will usually all go over in the first 50 c.c. of distillate, but the same quantity (i.e., 150 c.c.) must be distilled off in all cases in order that when the actual analysis of the water is started the condition as to volume may be constant.

In fact, it may be conveniently stated here that *perfect uniformity of conditions* is a requisite for success in water analysis

<sup>42</sup> For a description of the retorts, condensers, etc., used by the author, see pp. 62, 66, and 67.

To the contents of the retort is now added half a liter of the water to be examined.

Distil and catch the distillate in 50-c.c. Nessler tubes. The rate of the distillation should be so managed as to allow about ten minutes for the filling of each 50-c.c. tube.

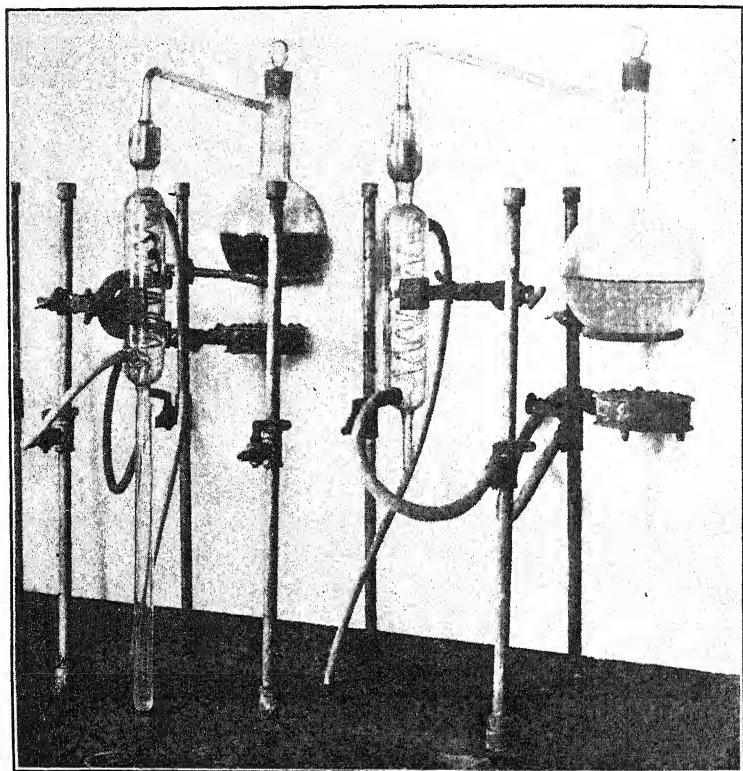


FIG. 8.—Ammonia Stills.

Add 2 c.c. Nessler reagent to each tubeful. Four tubes will be sufficient to carry off all free ammonia.

From a small burette measure definite amounts of the *standard ammonium chloride solution* into several clean Nessler tubes. Dilute each to the 50-c.c. mark with ammonia free water, add 2 c.c. Nessler reagent, and, after standing for ten minutes, compare as to depth of tint with

the distillates already Nesslerized. With a little practice it will be found easy, by varying the amounts of standard ammonia solution used, to produce tints corresponding to those existing in the distillates, and thereby an accurate knowledge of the quantity of ammonia actually present may be obtained. Such ammonia existed ready formed in the water, either free or as an ammonium salt, and passed over unchanged with the steam; it is therefore technically known as "*free ammonia*."

The author makes use of the following device for reading Nesslerized ammonia tubes.<sup>43</sup> The illustration shown on page 64 requires but little explanation. Two disks of brass  $\frac{1}{4}$  inch thick and  $6\frac{5}{8}$  inches in diameter are joined together by twelve tubes of brass  $\frac{13}{16}$  inch in inside diameter and  $9\frac{3}{4}$

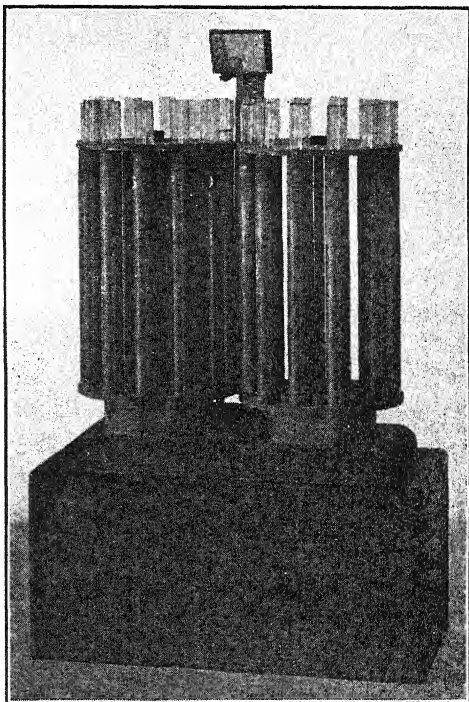


FIG. 9.—Nessler Camera.

inches in length. The glass Nessler tubes, which are  $\frac{3}{4}$  inch in diameter and 8 inches to the 50-c.c. mark, just fit these brass tubes and are kept from falling through the open bottoms by the holes in the lower brass disk being slightly smaller than the diameter of the brass tubes.

Each lower brass disk is furnished with a very short but

<sup>43</sup> Supplied by Emil Greiner & Co., New York.



broad pivot (3 by  $\frac{1}{4}$  inch), which fits into a socket on the wooden stand, thereby permitting the set of tubes to be rotated about a vertical axis. The wooden stand in question has a base of  $6\frac{3}{4}$  by  $13\frac{1}{2}$  inches, supporting the pair of wooden sockets. Between the sockets is a small

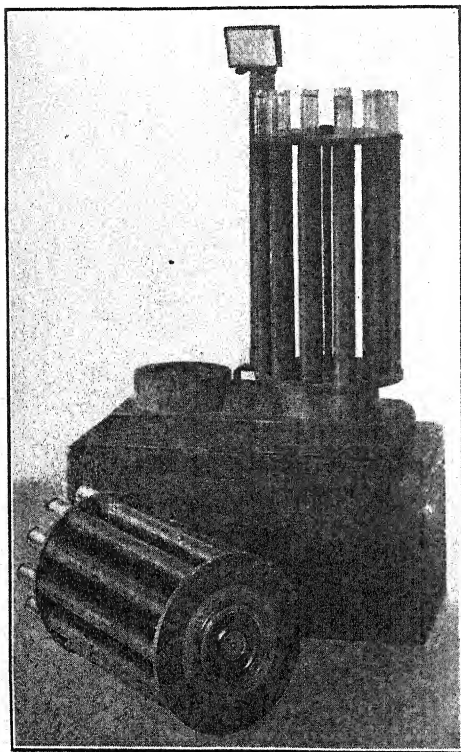


FIG. 10.—Nessler Camera (Showing Construction).

mirror set at an angle of 45 degrees, which throws light up through the two Nessler tubes under comparison, and permits the observer to see them in the upper mirror as though in horizontal position. The Nessler standards being placed in the set of tubes on the left and the "free and albuminoid" ammonias in the set on the right, the two sets can be rotated at will until the colors on the right hand are matched by those of the standards on the left.

To make clear the calculation of results it will be necessary to cite an example: Suppose the first tubeful to have required 9 c.c. standard ammonia solution (diluted to 50 c.c.) to match its color when Nesslerized, the second one 3 c.c., and the third 1 c.c. Then, since each cubic centimeter of the standard ammonia solution corresponds to .01 mg. N, the whole amount of "nitrogen as free

ammonia" present in the original half liter of water would be:

1°.....	0.09
2°.....	0.03
3°.....	0.01
4°.....	0.00
	<hr/>
	0.13 mg.

Multiplying this by two to obtain the quantity for an entire liter, and remembering that 1 mg. is the millionth part by weight of a liter of water, the total "nitrogen as free ammonia" present in the water will be .26 *part per million*.

**Permanent Standards.**—In laboratories where much work is done in water analysis it is very convenient to keep at hand sets of standards for quickly reading the Nesslerized ammonia tubes and also the colors obtained in the iron and other determinations. Such standards are prepared by diluting suitable mixtures of sundry colored solutions. Useful as they are to men of experience, it is questionable if it be wise to put them into the hands of students who may by their use lose sight of what the real standards are. The author objects to their employment in a laboratory of instruction for practically the same reason he opposes the too liberal use of factors in general quantitative analysis. For the convenience of analysts in routine laboratories, the directions for the preparation of permanent standards have been included in an appendix to the present edition.

#### NITROGEN AS ALBUMINOID AMMONIA

Throw out the residue remaining after the distillation for *free ammonia*, clean the retort thoroughly, and refit it to the condenser. Place in the retort 200 c.c. ammonia free water and 50 c.c. of the *alkaline permanganate solution*. Distil off three 50-c.c. tubes, and Nesslerize the third one in order to insure freedom from ammonia. Add half a

liter of the water under examination, and proceed with the distillation, and the Nesslerizing of the successive 50-c.c. portions of the distillate, as in the determination of *free ammonia*. The distillation is to be continued until five 50-c.c. tubes are filled. The ammonia determined by this distillation will be *total* (i.e., "free" plus "albuminoid"); therefore, from the Nessler reading of each tubeful of distillate must be subtracted the reading for the corresponding tubeful for "nitrogen as free ammonia": the difference will give the "nitrogen as albuminoid ammonia" for that tube.

The calculation is entirely similar to that for *nitrogen as free ammonia*, as stated.

It must be understood that the retorts and condensers hitherto described are such as would be found in a general laboratory and are not the best and most convenient for special water work. The "ammonia table" used by the author is pictured on page 62. The supports are all of piping. Those holding the retorts also carry gas for the lamps and those for the condensers convey the cooling water. Along the middle of the table are openings leading to the sewer to which the condenser water escapes. Connection between retort and condenser is made by a mercury seal.<sup>44</sup>

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In working the "albuminoid ammonia" process it is of importance that sundry minor details should be observed in order that concordant results may be obtained.

---

The Nessler tubes used are long and narrow, being  $11\frac{1}{2}$  inches total length, and 8 inches from the bottom to the 50-c.c. mark. They should always be rinsed with ammonia free water immediately before using. A very convenient lamp for heating the retorts is the broad flat Bunsen ( $3\frac{1}{2}$  inches diameter), with numerous small jets over its surface.

<sup>44</sup> All the glassware here described can be supplied by Emil Greiner & Co., New York.

Keep the current of cooling water passing through the condenser at a velocity such that the difference between the temperature of the inflowing and outflowing water shall not exceed  $1^{\circ}\text{C}$ .

---

Be very careful to have the "standard ammonia" solutions and the distillates at the same temperature when the Nessler reagent is added; otherwise equal strengths of ammonia would strike different shades of color and produce error. This end is best achieved by allowing the distillates to attain the temperature of the room before adding the Nessler reagent. Daylight is best for reading Nessler colors, but if necessary a Welsbach burner may be used.

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Even with the utmost precaution some ammonia will be lost through imperfect condensation, and this loss will be greater in proportion as the rate of distillation is made more rapid.

---

The amount of ammonia in the distillate being a function of the time employed, it becomes necessary to eliminate, so far as may be, any error that might arise from this source by conducting all distillations as nearly as possible at the same rate. So manage the lamp, therefore, as to fix the time required for the distillation of each 50 c.c. at *ten minutes*.

---

It is not sufficient to note the *total* amount of "free" and "albuminoid" ammonias, but the full notes of the Nesslerizing process must be retained, that the *rate* at which the ammonia passes over may be observed (see p. 62).

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Do not observe the tint of a Nesslerized solution until ten minutes after the addition of the reagent. After the expiration of that time the color may be considered constant, no further material change taking place in twelve hours. Consequently, in the case of the examination of

many successive samples, the Nesslerized standard solutions need not be made up for each water, but those prepared in the morning may be used during the entire day, proper care being taken to protect them from the action of the atmosphere by covering them when not in use.

The routine standards are: .00, .0025, .005, .0075, .01, .015, .02, .03, .04, .05, .06, and .07.

Higher colors than these cannot be read with accuracy. Should the ammonias run beyond the highest of these standards, remove a definite amount from the Nessler tube, dilute it to the 50-cc. mark, compare with the routine standards, and allow for such dilution.

Much trouble was formerly experienced from the low standards becoming clouded or "smoky." This was found to have been due to the fact that, in making the distilled water, the water in the copper retort had been allowed to run too low, resulting in volatile decomposition products being evolved from the concentrated organic matter.

Occasionally a citron-green color is produced which masks the ammonia reaction and renders its estimation difficult. Dr. Kidder of the navy observed this interference with the ammonia coloration, and attributed it to the presence of substances evolved in the putrefaction of organic matter. He concluded from the few experiments he made that the amines are not necessarily concerned in its production, as he found that butyric acid gave a somewhat similar interference to that met with.<sup>45</sup>

As has already been pointed out, water samples will not keep long; whence the necessity for a speedy analysis after the collection is once made.<sup>46</sup>

With many waters the tendency is for "free ammonia" to disappear upon keeping; and, as a rule, the "albuminoid ammonia" also diminishes, but this rule is by no means uniform." For instance, the author found that a certain

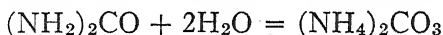
<sup>45</sup> Reference Handbook of the Medical Sciences, p. 157.

<sup>46</sup> The changes which take place in water upon keeping have been carefully investigated by Smart and Mallet (Nat. Board of Health, 1882).

brown water, after ten days' storage, showed an increase in "free ammonia" from .125 to .28 and a decrease in "albuminoid ammonia" from .255 to .235. The equations for the hydrolysis of proteins by bacteria have been given by Robinson (J. Biol. Chem. 30, 135) as follows:



Urea hydrolyzes easily according to the equation



These equations indicate steps in the "cycle of organic nitrogen."

From observations made upon the appearance and disappearance of nitrates there seems to be little doubt that the loss of "free ammonia" is to be accounted for by a process of nitrification. Nitrites are formed at the expense of the ammonia, and they, in their turn, are converted into nitrates, by further oxidation. Nitrogenous organic matter in water may be considered as belonging to two classes: *first*, "that which passes readily into the condition of 'free ammonia' through putrefactive agencies," and which is consequently easily acted upon by the alkaline permanganate solution; and, *second*, that which is more stable, and from which no ammonia is evolved during distillation with this reagent. Upon standing for any considerable time this latter class becomes slowly converted into the less stable variety, which, in its turn, is gradually converted, at least in part, into "free ammonia," the ammonia in turn becoming finally nitrified, as already stated. Thus we have a perfect system of changes, from the stable nitrogenous organic matter on the one hand to the fully oxidized nitrate on the other. Of course we are citing but a typical case, and must be prepared to see all manner of departures therefrom in special instances, according as the character and amount of materials and the nature of the environment may differ.

If the albuminoid ammonia be redetermined after the sample has stood a number of days an idea might be obtained of the stability of the nitrogenous organic material whence such ammonia was derived.

Should hydrogen sulphide be present in the water it would pass into the distillate and react with the Nessler reagent. In such a case add enough lead salt to react with the  $H_2S$  in the sample before distillation.

**Interpretation of Results.**—Concerning the interpretation of results, Wanklyn, the originator of the method, is very dogmatic, and says: "The analytical characters, as brought out by the ammonia process, are very distinctive of good and bad waters, and are quite unmistakable. There is, indeed, hardly any branch of chemical analysis in which the operator is less exposed to the risk of failure."

This statement is altogether too strong. Waters of high organic purity or those of gross pollution are relatively easy to classify, but with the numerous cases which lie about the boundary line between "good" and "bad" the greatest care is to be exercised in the reading of results and the passing of judgment. One rule, already mentioned, and upon which too much stress cannot be laid, is never to give an opinion concerning a water the history and surroundings of which are not thoroughly known.

As an illustration of variation in the ammonias, the following data are offered (see also p. 7):

	Free Ammonia. P.p.m.	Albuminoid Nitrogen. P.p.m.
Average in sundry surface waters known to be pure.....	0.063	0.066
Average in sundry surface waters known to be polluted.....	.182	.228
Average in sundry ground waters known to be pure.....	.009	.007
Average in sundry ground waters known to be polluted.....	.107	.081

The "free ammonia" in artesian wells is often excessive

under circumstances that make animal contamination an impossibility, and even rain water, freshly collected after periods of long drought, will often exhibit properties calculated to mislead the analyst.

C. B. Fox gives the following determinations in pure *deep well* waters:

	Free Ammonia. P.p.m.	Albuminoid Nitrogen. P.p.m.
Well 230 feet deep.....	0.80	0.05
“ 250 “ .....	.76	.04
“ 300 “ .....	.74	.03
“ 330 “ .....	.37	.06
“ 385 “ .....	.59	.04
“ “very deep”.....	.41	.07

✓ This excess of free ammonia may be due either—

1. To entrance of rainwater;
  2. To the beneficial transformation of harmful organic matter into the harmless ammonia, through the agency of sand, clay, and other substances which act on the water in a manner similar to the action of a good filter.
  3. To some salt of ammonia existing in the strata through which the water rises; or,
  4. To the decomposition of nitrates in the pipes of the well.
- Mr. H. Slater suggests that the agent concerned in this reduction may, in the case of the deep well waters, be the sulphide of iron which is found in the clay.

“We conclude, then, that the presence of free ammonia in such comparatively large quantities in these deep well waters is due to the reduction of nitrates and nitrites by sulphide of iron, or some kinds of organic matter, or some other agent, such oxidized nitrogen salts having been produced in past ages by the oxidation of organic matter.”<sup>47</sup>

Free ammonia in deep well water may, however, be derived from very objectionable sources; as when surface pollution is admitted because of cleavage and fracture

<sup>47</sup> Fox, Sanitary Examinations of Water, Air, and Food.



cracks in friable rocks, and because of the "dip" of the strata being nearly vertical. "The author has seen numbers of such cases.

Take, for instance, the water from a rock-drilled well in friable shale. The boring was 57 feet deep and was located in a city containing many privy vaults, the nearest of which was 75 feet distant. The "free ammonia" reached the very high figure of 2.025, and curiously enough there was no "albuminoid nitrogen" whatever. An additional item condemning this water was the large amount (69 p.p.m.) of chloride present.

Free ammonia is at times very high in the rainwater collected near large cities, and is liable to run higher in winter than in summer. Of course high figures under such conditions are without objection, assuming a clean roof and a clean cistern; but when dealing with rainwater it must be always borne in mind that storage cisterns are often very foul.

Dr. Drown points out the low values commonly found for both "ammonias" in ground waters of good quality, and places that for albuminoid nitrogen as rarely exceeding .025. He shows the influence of growing plants in reducing free ammonia in surface waters, and quotes as illustration the great difference in this item in the water of Mystic Lake with change of season; thus two readings for free ammonia were:

August.....	0.000
January.....	.573

A further point that is mentioned by the same observer is the liability to high free ammonia readings in water from wells sunk in ferruginous, swampy regions, because organic matter associated with oxide of iron furnishes in absence of oxygen favorable conditions for development of ammonia.<sup>48</sup>

Water passed through newly laid and rusty mains will

<sup>48</sup> Mass. Board of Health, 1892, 324.

often become materially changed in chemical character as well as in physical appearance. The influence of the iron rust is to reduce the nitrates present and increase the nitrites and free ammonia. A good water might thus be very readily condemned upon the analytical results alone did the analyst not know its antecedents.

Wanklyn would clear away all difficulty of interpretation by holding that "albuminoid nitrogen above .10 p.p.m. begins to be a very suspicious sign; and over .15 it ought to condemn a water absolutely." Such a hard-and-fast rule is too severe for general application.

Many an excellent water is seen to greatly exceed these limits, particularly the brown waters supplying some of our Eastern towns. Numerous peaty waters, of proved wholesomeness, far exceed them. As has already been pointed out, waters of a brown or peaty character are always to be looked upon very narrowly, but many of them are unquestionably of good quality, and all of them would be condemned by the proposed standards.

The analyst must here again use his good judgment and decide whether or not there is natural and harmless cause for the high ammonia readings. The depth of color of the water will be a material guide to his decision.

The analysis of the water from a mountain lake situated far away from all possibility of sewage contamination, gave the following results:

Free ammonia.....	0.01 p.p.m.
Albuminoid ammonia.....	.34

An excellent mountain stream recommended for a city supply, although but slightly colored, ran:

Free ammonia.....	0.055
Albuminoid ammonia.....	.230

As a result of the analysis of fifteen drinking waters from widely scattered sources, many of them city supplies, and all of them believed to be wholesome, Prof. Mallet

gives figures for "albuminoid nitrogen" that show an average of .152 p.p.m. (highest = .325, lowest = .020). Most of these would be condemned by the Wanklyn standard.

Some years ago Dr. Smart pointed out that the *rate* at which the ammonia is evolved is of an importance at least equal to, if not greater than, the total amount; he holds that: "*Gradual* evolution of albuminoid ammonia indicates the presence of organic matter, whether of vegetable or animal origin, in a fresh or comparatively fresh condition, while *rapid* evolution indicates that the organic matter is in a putrescent or decomposing condition."

This is entirely in accord with present experience. Thus the evolution of albuminoid ammonia was found as follows when analyzing the water of a mountain lake in which was a considerable growth of pond lilies and other water plants:

Nessler tube No. 1	0.0600
" " 2	.0450
" " 3	.0250
" " 4	.0150
" " 5	.0100
" " 6	.0075
" " 7	.0050
" " 8	.0025

---


$$0.1700 \times 2 = 0.34 \text{ p.p.m.}$$

Water giving such results can be looked upon with much more favor than one presenting an albuminoid record such as the following:

Nessler tube No. 1	0.1000
" " 2	.0350
" " 3	.0125
" " 4	.0025
" " 5	.0000

---


$$0.1500 \times 2 = 0.30 \text{ p.p.m.}$$

Thus we see that the interpretation of results is entirely a question of opinion and sound judgment, and in this connection Mallet's conclusion cannot be read without marked interest; he says: "It is impossible to decide absolutely upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of the processes for the estimation of organic matter or its constituents. I would even go further, and say that, in judging the sanitary character of a water, not only must such processes be used in connection with the investigation of other evidence of a more general sort as to the source and history of the water, but should even be deemed of secondary importance in weighing the reasons for accepting or rejecting a water not manifestly unfit for drinking on other grounds. There are no sound grounds on which to establish such general standards of purity as have been proposed."

As a further aid to judgment, analyses of sundry waters in different parts of the country are given on the next page, several of them having caused disease. Also a few instances of waters of reliable quality including certain city supplies. As elsewhere throughout the book, the results are in parts per million.

It will be observed that several of the impure waters quoted have figures for free ammonia higher than those for albuminoid ammonia. This is always a suspicious sign, unless both numbers in question be low.

One of the worst waters in the list, number two, would not have been condemned upon the ammonia items at all, thus showing the importance of judging from the completed analysis. Water number three was from a well drilled in friable shale and within short distance of city privies. Water number four was from an isolated country summer residence. The water is materially higher in "chloride" and "nitrates" than the local "normals," and is exposed to drainage from outhouse and stables.

Water number nine was from a well drilled into Hudson River shale, and protected from immediate surface drain-

age. The chloride rose from 58 to 64.3 some fifteen hours after emptying a bushel of salt into a privy vault 50 feet distant.

Number.		Free Ammonia	Albuminoid Ammonia	Chloride	N as Nitrate	N as Nitrite	Required Oxygen	Total Solids
Poor quality	1 Shallow city well.....	0.025	0.08	122	17.38	trace	1.4	554
	2 City well 30ft. deep (caused typhoid).....	.005	.035	146	10	0	1	769
	3 Rock-drilled city well 57 ft. deep.....	2.025	0	69	.025	0	0.85	487
	4 Spring water (caused repeated cases of dysentery).....	.01	.025	6	7	0	0.8	35
	5 Well near city.....	.005	.045	24	9	0	1.1	215
	6 City well.....	.4	.04	93	1.5	.005	.....	380
	7 Town well.....	.815	.075	36	0	trace	.....	421
	8 City well 250 ft. deep.....	1.59	.395	102	0	trace	.....	681
	9 City well 255 ft. deep.....	.31	.02	58	0	0	6.45	635
	10 City well 226 ft. deep.....	1.11	.08	199	0	0	1.3	779
	11 Deep well in large stockyard, Kansas City.....	1.725	.025	80	0	trace	.....	.....
	12 Hudson River, at Troy, during freshet.....	.42	1	3	.5	trace	.....	205
	13 Deep city well, in "made ground".....	excessive	excessive	47	.875	0	2.5	637
	14 Hudson River, near Albany, N. Y.....	.078	.346	1.87	.44	.008	14.4	125
	15 Mohawk River, near Cohoes, N. Y.....	.104	.176	2.25	.6	.002	6.8	137
	16 Niagara River, Niagara Falls.....	.036	.122	7.25	.12	.001	2.9	152
Good quality	17 Town supply, Elizabethtown, N. Y. (brook)...	0.048	0.002	1.05	0.05	0	0.35	106
	18 Lake Placid, N. Y.....	.022	.052	0.75	.50	.001	1.3	192
	19 Syracuse, N. Y. (lake water).....	.012	.020	1.5	.36	.003	1.8	122
	20 Wachusett Res., Boston...	.022	.143	2.8	.03	0	4.0	34.8
	21 Pittsfield Res.....	.026	.161	1.0	.01	0	4.0	32.7
	22 Kensico Res., New York City.....	.005	.055	1.5	.10	.002	.....	58
	23 Peaty mtn. stream (autumn).....	.055	.23	2.4	0	0	7.4	34
	24 Same stream in winter.....	.055	.117	1.9	.08	0	6.6	47
	25 High mountain lake (peaty).....	.01	.34	2	0	0	6.6	43
	26 Lake Erie (middle of lake).....	.045	.112	3.5	.08	trace	1.25	134
	27 Lake Superior (40 miles from shore).....	.03	.02	1	.1	0	1.15	54
	28 Large well-situated spring.....	.027	.006	2.2	1.6	0	0	90
	29 Mountain spring.....	.04	.048	4	1.404	trace	.3	228
	30 Domestic well (Catskill Mountains).....	.016	.007	.75	.175	0	.35	32
	31 Flowing wells (N. J. coast).....	.023	.05	9	.5	trace	.4	30
	32 Driven wells (Hempstead, N. Y.).....	.013	.004	2.5	1.25	0	.35	22
	33 Schenectady, N. Y. (ground water).....	.016	.016	4.5	.50	.001	1.3	192
	34 Lowell, Mass. (ground water).....	.300	.058	3.6	.22	.001	.....	59.8
	35 Brookline, Mass. (ground water).....	.052	.070	7.5	.19	.001	.....	86.9
	36 Middleboro, Mass. (ground water).....	.055	.062	6.8	.43	0	.....	65.8
	37 North Woods Club, Remote forest spring.....	0	.020	2.0	.28	trace	.25	83

Water number ten was from a drilled well, in shale rock, constructed with much more care than usual. Extreme precautions were taken to shut out all immediate surface drainage, and they were undoubtedly successful. Nevertheless, the neighboring privies contributed their seepage, raising the "free ammonia" and "chloride" tremendously above the local "normals." Such results show us how unsafe it is to trust to the purity of rock-drawn water, when, owing to the seamy character of the rock, and the direction and angle of its "dip," almost direct connection may be established between the bottom of the well and the surrounding sources of surface pollution.

The bore hole in some rocks, if not in all, is not truly circular in section and opportunity is presented for pollution to flow down in the space between the well casing and the rock wall, thus reaching the bottom of the well. In this connection the author recalls a remark frequently made by G. C. Habermeyer, for many years engineer of the Illinois State Water Survey, to the effect that "ninety-nine per cent of the sources of pollution are to be found within three inches of the top of the well."

A comparison of waters twenty-three and twenty-four shows the influence of freezing weather in tying up the fountains of "peaty" contamination.

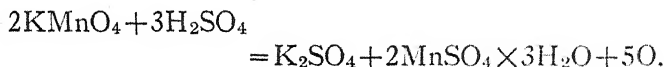
#### OXYGEN-CONSUMING CAPACITY

(Required Oxygen)

This determination (which must not be confused with that of "dissolved oxygen" nor with "biochemical oxygen demand") deals principally with the carbon present in the organic matter and is Kubel's modification of the old permanganate process of Förschhammer. The original mode of procedure was published in 1850, and "consisted merely in adding a solution of potassium permanganate of known strength, without any other reagent, to a measured amount of water to be examined, until the liquid had acquired a faint permanent tinge, and then noting the quantity used.

It was afterward ascertained that more uniform results could be obtained, and with less expenditure of time, by causing the permanganate to act in the presence of free acid or free alkali." Kubel uses a boiling temperature. The reagents required are:

**Standard Potassium Permanganate Solution.**—Dissolve .3951 gram of the salt in one liter of distilled water. Each cubic centimeter of such solution will contain .1 mg. of oxygen available for oxidation. The available oxygen of the permanganate in presence of sulphuric acid may be represented by the equation



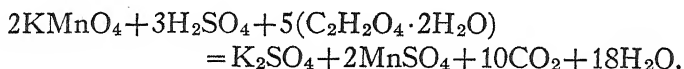
If a high quality of permanganate is not available, it will be convenient to weigh out about 1 per cent more than the theoretical amount given and standardize the solution against a freshly prepared solution of pure sodium oxalate.<sup>49</sup> If possible, it is advisable to allow a solution of permanganate to stand for two weeks and then decant through an asbestos filter before standardization. A solution prepared in this way will hold its titer for some months, if protected from the light.

**Dilute Sulphuric Acid.**—One part of the strong acid to three of distilled water.

**Solution of Oxalic Acid** ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ).—Dissolve 0.7753 gram of the crystallized acid in one liter of distilled water. An equivalent amount of ammonium or sodium oxalate may be used instead of the oxalic acid. The "dust" from oxalic acid or oxalates is injurious if inhaled. This solution if titrated against the permanganate solution (while hot and in presence of  $\text{H}_2\text{SO}_4$ ) should correspond to it

<sup>49</sup> McBride, R. S., Standardization of Potassium Permanganate Solution by Sodium Oxalate: Bull., Bureau of Standards, 8, 612.

cubic centimeter for cubic centimeter. In practice, however, this correspondence will be found to be approximate only. The equation is



The solution tends to grow weaker quite rapidly with lapse of time, and must be restandardized every time it is used. This is, however, but a slight inconvenience, and is accomplished as follows:

Ten c.c. of the oxalic-acid solution, diluted with 100 c.c. distilled water and 10 c.c. of the dilute sulphuric acid, are titrated, boiling, with the standard potassium permanganate solution, and the amount of the latter required to produce a faint pink tinge is recorded.

**Determination.**—Place 100 c.c. of the sample in a 250-c.c. Erlenmeyer flask and add 10 c.c. of the dilute sulphuric acid. Heat rapidly for 30 min. in a steam or water bath and run in the standard permanganate solution from a burette until the water has a marked red color. Continue heating, adding more permanganate from the burette from time to time, if necessary, in order to maintain approximately the intensity of red color observed at the start. Do not let the color fade nearly out, and then add the permanganate in quantity, but strive to keep the color as nearly constant as possible by gradual addition.

Remove from the bath, add 10 c.c. (or more, if necessary) of the oxalic-acid solution to destroy the color, and then add the permanganate solution, from the burette until a faint pink tinge again appears. From the total permanganate used deduct that corresponding to the 10 c.c. (or more) oxalic acid employed, and from the remainder calculate the milligrams of "required oxygen" consumed by the organic matter present in the water. Correction must be made for nitrites, ferrous salts, or hydrogen sulphide, if any of them be present.



<i>Example:</i>	c.c.
Total permanganate solution used.....	25.
Less that required for the oxalic acid.....	9.7
Hence that required to oxidize organic matter (corresponding to 1.53 mg. oxygen).....	15.3

Therefore, "required oxygen" is  $1.53 \times 10 = 15.3$  p.p.m. Since this is an empirical test it is essential that the relative concentrations in the final reaction mixture be held within rather narrow limits. When highly polluted samples are to be tested it is better to use a stronger standard  $\text{KMnO}_4$  solution than to dilute the sample. British chemists use a temperature of  $80^\circ \text{F}$ . for four hours as standard procedure.<sup>50</sup>

**Comparates.**—As this determination deals principally with the organic carbon present, the readings are naturally high in the cases of brown, peaty waters and surface waters carrying organic matter in suspension. (See the list of analyses, p. 76.)

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Average in sundry surface waters known to be pure.....	1.58 p.p.m.
Average in sundry surface waters known to be polluted.....	3.00
Average in sundry ground waters known to be pure.....	0.31
Average in sundry ground waters known to be polluted.....	1.06

Averages from determinations by Dr. Smart:

Impure (14 samples).....	5.880 p.p.m.
Doubtful purity (5 samples).....	3.073
Medium purity (15 samples).....	1.414
Pure (18 samples).....	0.581

The severe character of the following French classification is due to the fact that spring waters are popular in France, and surface waters are filtered before use:

Very pure.....	1 p.p.m.
Potable.....	2
Suspected.....	3 to 4
Impure.....	above 4

<sup>50</sup> Purvis and Hodgson, *The Chemical Examination of Water Sewage and Food*: Cambridge Public Health Series.

In the opinion of the author the determination of "required oxygen" does not furnish information of great value. Deeply colored waters, otherwise pure, are sure to give high results, because of the quantity of carbon present, and a simple inspection, with measurement of the color, would give equally valuable information. The test has its greatest usefulness in the study of heavily polluted samples whose source alone condemns them for drinking purposes.

#### LEAD AND COPPER

For the accurate determination of either lead or copper considerable quantities of the water should be evaporated and the residue then examined by the scheme to be found in works on general quantitative analysis. For the approximate estimation, which is often sufficient, the ease with which their dark sulphides may be formed provides a ready method (Miller).

Prepare a *standard solution of lead nitrate*,  $\text{Pb}(\text{NO}_3)_2$ , by dissolving 1.599 grams of the salt in one liter of distilled water. Each cubic centimeter will contain 1 mg. metallic lead.

Precipitate metallic copper electrolytically in a platinum dish, weigh, dissolve it in a few drops of  $\text{HNO}_3$  and dilute with sufficient water to allow each cubic centimeter of the solution to contain 1 mg. metallic copper. Use this as the *standard copper solution*.

Place the water in a 100-c.c. Nessler tube, slightly acidify with acetic acid, pass  $\text{H}_2\text{S}$  and match the tint by operating in a similar manner with measured amounts of the standard lead or copper solution diluted to 100 c.c.

Ammonium sulphide solution may be substituted for  $\text{H}_2\text{S}$ . One or two drops of a good solution will be sufficient.

This method will not, of course, distinguish between copper and lead, but distinguishing is not commonly necessary.

High natural color or the presence of iron in the water interferes with the determination.

The accurate determination of small amounts of lead involves a tedious and difficult procedure which should be carried out by a thoroughly trained chemist. Directions will be found in Standard Methods of the American Public Health Association or the A. O. A. C. Since the allowable limit for lead is .1 p.p.m. and for copper is .2 p.p.m., any darkening of the sample with the addition of sulphide should be regarded with suspicion and further investigation made.

For the detection of copper in water which has been treated with copper sulphate for algæ removal, a convenient test is the following:

Concentrate if necessary.

Add a few drops of formaldoxime<sup>51</sup> (prepared by dissolving 1 part of hydroxylamine hydrochloride in 5 parts of formaldehyde).

Add some strong KOH solution.

A violet color indicates copper.

The color fades quickly and must be matched at once for quantitative purposes.

### IRON

This metal is objectionable if present in considerable quantity, particularly in water to be used for washing white goods and for dyeing. A knowledge of the presence of iron, moreover, will aid in guarding against an invasion of crentothrix.

The *standard of iron solution* is prepared by dissolving .1 gram pure iron in a little HCl to which a few drops of HNO<sub>3</sub> have been added, evaporating to dryness, moistening with HCl, and then diluting to one liter. One c.c. of this solution will contain .1 milligram of iron.

If more convenient, pure ferrous ammonium sulphate crystals may be weighed out in amount equivalent to the pure iron specified. In this case the salt should be dis-

<sup>51</sup> Trans. Chem. Soc., 1898.

solved in 75 to 100 c.c. of 2N sulphuric acid (1 part ordinary dilute acid plus 2 parts water) and oxidized with  $\text{KMnO}_4$  before diluting to a liter.

**Determination.**—Take 100 c.c. of the water; evaporate to dryness; ignite at low redness sufficiently to decompose organic matter; add 1 c.c. 3 N HCl; warm, dilute slightly, filter if necessary and wash; dilute to 100 c.c. in a Nessler tube, add a few drops of  $\text{KMnO}_4$  solution (5 grams per liter) to make the slight pink color persist five minutes; add 5 c.c. KCNS solution (20 grams per liter), and compare the depth of color produced with those formed by known amounts of standard iron solution which have been diluted and treated in the same way with similar quantities of HCl,  $\text{KMnO}_4$  and KCNS.

The standards must be made at the same time because time is an element in this determination. The red color produced tends to pale out even after a few minutes' standing. Comparison must be made at once.

Iron which tends to increase in a well water as the draught upon the underground supply grows in volume is a discouraging symptom; for the probabilities are strong that the water will eventually become unfit for use unless the ever-increasing iron be artificially removed.

At Lowell, Mass., the changes in the iron content of the driven well-water were:

1896-00.....	0.322 p.p.m. Fe
1901-05.....	.341 "
1906-10.....	.770 "
1911-13.....	1.468 "

Finally an iron-removal plant had to be established.<sup>52</sup>

In his *Filtration of Public Water Supplies*, p. 186, Hazen writes: "Three-tenths of a part per million of metallic iron very rarely precipitates or causes any trouble."

As the result of wide inquiry among those interested in

<sup>52</sup> See Barbour's report to the Municipal Council, 1914.

water for laundry purposes, the author concludes that iron to the extent of .25 p.p.m. may be considered satisfactory; more than .5 p.p.m. unsatisfactory; and the values between doubtful.

In this connection note the conflicting statements made by the following Massachusetts communities (the figures given indicate the amounts of iron in the several waters):

Methuen.....	0.365	satisfactory
Grafton.....	0.507	"
Newburyport.....	0.720	"
Cohasset.....	0.380	not satisfactory
Hyde Park.....	0.859	

It is well to note in this connection that it takes .1 to .3 p.p.m. of iron in solution (not colloidal nor suspended) to sustain a growth of crenothrix.

The decision as to whether or not treatment for the removal of iron is necessary will depend largely on local sentiment. If such a plant is installed, it should be required to deliver a water containing less than .1 p.p.m. of Fe.

### ZINC

Zinc is not a cumulative poison, nevertheless its presence in a water is undesirable. Galvanized iron pipe is attacked by certain waters, especially those that are soft, and spring water is at times zinc-bearing, as has been especially noticed in Southern Missouri.

For the determination of the metal in absence of lead, copper, and manganese, evaporate three liters of the water to dryness in presence of HCl.

Bake for an hour at 110° C. Moisten with HCl, add water and filter off SiO<sub>2</sub>. Make alkaline with NH<sub>4</sub>OH, boil and filter off the hydroxides of iron and aluminum. Dissolve the precipitate in a little HCl and reprecipitate it with NH<sub>4</sub>OH. Filter and reject the precipitate. Unite the two filtrates. Boil off the ammonia. Make acid with acetic acid, and while still hot pass H<sub>2</sub>S. Let the pre-

## ZINC-BEARING WATER FROM MISSOURI\*

	Parts per Million.		Parts per Million.
PbSO <sub>4</sub> .....	trace	CaSO <sub>4</sub> .....	109.9
CuSO <sub>4</sub> .....	0.5	MgSO <sub>4</sub> .....	19.0
CdSO <sub>4</sub> .....	0.9	K <sub>2</sub> SO <sub>4</sub> .....	5.6
ZnSO <sub>4</sub> .....	297.7	Na <sub>2</sub> SO <sub>4</sub> .....	5.9
FeSO <sub>4</sub> .....	1.6	NaCl.....	4.3
MnSO <sub>4</sub> .....	6.3	CaCO <sub>3</sub> .....	72.0
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	2.5	SiO <sub>2</sub> .....	13.7
			539.9

\* Hillebrand, Bull. 113, U. S. Geol. Survey.

precipitate settle. Filter and dry. Remove the precipitate from the paper. Ignite the paper in a porcelain Rose crucible. Add the precipitate and ignite for fifteen minutes in a stream of H<sub>2</sub>S. Ignite sulphide in air at 930° C. for forty-five minutes and weigh as ZnO. Ignite residue at low heat, then cool, moisten with H<sub>2</sub>SO<sub>4</sub>. Reignite at 385-400 degrees to expel H<sub>2</sub>SO<sub>4</sub>, and weigh as ZnSO<sub>4</sub>.

For qualitative purposes, Allen's test is useful: Acidify the clear water with HCl; make slightly alkaline with ammonium hydroxide; boil; filter, and add a few drops of potassium ferrocyanide. A white precipitate will form in presence of a trace of zinc.

When applying this test it must be remembered that only the zinc in solution is detected. That portion which is present in insoluble form, suspended in the water, is often the larger of the two.

When the necessary equipment is available, electrolytic methods are convenient. Such methods are described in recognized texts on chemical analysis as well as in Standard Methods.

Reports recording that a water contains so many parts per million of lead, zinc, or other metal are common enough, but it is rare to find advance statements of what a water is capable of doing in the way of dissolving metals should

opportunity be afforded it of coming into contact with them. In other words, a client who possesses a water supply which is very desirable at its source is seldom informed of the possible damage which may result thereto by reason of its being conveyed through metallic piping.

After the pipes have been laid and the water admitted to them, record is made of the result as to the metallic solvency, but little is found in the nature of a prophecy antedating the outlay of capital; which prophecy, had it been uttered in time, might have had material bearing upon the investment. Again, if, as occurs in a few instances, the client be told that the water under examination is capable of acting upon certain metals, he is seldom given the information in such quantitative form as will enable him to make comparisons between it and other waters with reference to this property.

It is well known that all waters do not equally possess the power to attack metals and it is proper to ask that, granting that such power does exist, how far is its exercise objectionable from a sanitary point of view; or, to state it differently, what amount of metallic salts in solution may be allowed with safety?

There is some difference of opinion among the authorities as to the amount of contained lead required to condemn a water, but all are agreed that even small quantities should be narrowly watched. Thus, the Massachusetts reports note that one-half part per million has caused serious injury.<sup>53</sup> Haines holds that .1 grain per United States gallon (1.71 per million) should cause a water to be rejected.<sup>54</sup>

Whitelegge believes that "no water should be used for drinking which contains more than one part of lead per million, and any trace, however minute, indicates danger." (Hygiene and Public Health.)

<sup>53</sup> Mass. State Board of Health, 1898, xxxii.

<sup>54</sup> J. Fk. Inst., Nov., 1890.

Middleton considers 1.4 p.p.m. of either lead or copper sufficient to condemn a water.<sup>55</sup>

To quote Dr. Summerville in his recent paper in *Water*: "Lead to the extent of .25 p.p.m. is sufficient to condemn a potable water."

In four cities of Massachusetts where lead poisoning was produced, the average amount of the metal present during ordinary daytime use was one part or more per million. Occasional instances of "plumbism" were noticed in other towns and doubtless mild or unrecognized cases occurred elsewhere.<sup>56</sup>

In the thirty-first annual report of the London Local Government Board (1901 and 1902 Supplement on Lead Poisoning and Water Supply, Vol. 2, p. 426), peaty moorland waters are shown to be especially plumbosolvent, to a degree chiefly governed by the amount of acidity present, and experiments show that such acidity is due, at least in part, to acid-forming bacteria residing in the peat.<sup>57</sup>

The London report is so firm in its belief that the cause of plumbo-solvency had been located that it ventures to rate the moorland waters as "safe" if they are neutral to lacmoid and as "dangerous" if they react acid with that indicator.

H. W. Clark observed that carbonic acid in a soft water was the main factor that caused lead to be taken into solution by the waters of Massachusetts.<sup>58</sup>

It is by no means new to distinguish between the "solution" of lead and that "erosion" of the metal which some waters exercise whereby insoluble lead salts are formed with appreciable increase in the turbidity of the water.

For our purposes it will suffice to note that "erosion"

<sup>55</sup> *Water Supply*, p. 21.

<sup>56</sup> *Mass. State Board of Health*, 1898, p. 543.

<sup>57</sup> Cf. Thresh, *Examination of Waters*, p. 129 (3rd Ed.).

<sup>58</sup> *Engineering News*, Dec. 1, 1904.



does not occur in the absence of oxygen, and we are also to remember that from the sanitarian's point of view "erosion" may be fully as objectionable as "solution" if no opportunity for clarification be furnished. In fact, the former may readily be the greater evil of the two, because of its involving the possibility of the ingestion of large quantities of lead salts held in suspension.

Elder and Rees<sup>59</sup> have recently pointed out that the presence of chlorides greatly increases the rate at which lead is attacked.

The author believes that no water to be used for drinking purposes should contain lead compounds in quantity greater than what would correspond to one-tenth of a part per million of metallic lead.

Piping water in tubes of galvanized iron is very common, and as zinc is often more easily attacked than lead it is pertinent to ask if it be equally dangerous. So far as present experience can guide toward a correct solution of this question, the reply must be a negative one and the following opinions are presented in support of such contention:

In the journal of the German Society of Gas and Water Engineers for 1887, H. Bante collected statistics to show "that the use of galvanized pipes should be in no way detrimental to health."

Similar views are entertained by V. Ehmann, director of the water supply of Württemberg.<sup>60</sup>

According to Thresh<sup>61</sup> "there is no doubt that waters containing traces of zinc are used continuously for long periods without causing any obvious ill effects. The water supply to a small hospital with which I was connected for some years always contained a trace of zinc, probably never more than half a grain of the carbonate per imperial gallon (7.1 p.p.m.), but I never observed any indications

<sup>59</sup> Rees and Elder, *The Effect of Certain Illinois Waters on Lead*, J. Am. Water Works Assoc., 19, 6, 714 (1928).

<sup>60</sup> J. Fk. Inst., 1890.

<sup>61</sup> Op. cit.

of its being deleterious, although such effects were looked for."

In the Massachusetts Board of Health report for 1900, p. 495, the following table is given showing amounts of zinc in sundry public supplies, the metal having been dissolved from pipes of galvanized iron or brass during ordinary use. The results are averages and are in parts per million:

West Berlin.....	18.46
Milbury.....	3.08
Newton.....	1.25
Marblehead.....	0.85
Grafton.....	0.73
Wellesley.....	0.68
Fairhaven.....	0.52
Lowell.....	0.33
Webster.....	0.28
Sheffield.....	8.65
Palmer.....	2.90
Beverly.....	2.71
Fall River.....	0.07

The first, West Berlin, drew its water through 4000 feet of galvanized iron pipes. The quantity of metal dissolved therefrom was certainly large, but appears to have produced no evil results. "As far as is known the amount of zinc present in these waters as used is not sufficient to have any effect upon the health of the consumers of the water.

"The board has investigated the question of the presence of zinc in drinking-water supplies where galvanized iron pipes are used, and except in case of the use of some ground waters, containing very large amounts of free carbonic acid, which dissolves zinc and many other metals very freely, the amount of zinc found in ordinary water supplies, where galvanized pipes are used, is not sufficient, in the opinion of the board, to give anxiety."<sup>62</sup>

<sup>62</sup> Mass. State Board of Health, 1902, xliii.

In a private letter of more recent date the president of this board writes: "If there had been any harmful effects of the presence of zinc in the public drinking waters of the state that fact would have undoubtedly been brought to our attention. No statement to this effect had been made, nor has there seemed to this board reason suspecting serious danger from this source."

As an instance of long continued use of a water containing much zinc, the case of Brisbane, Queensland, should be quoted. In that city rainwater tanks built of galvanized iron are found in all the houses. The water, which is in common use, contains about 17.1 p.p.m. of zinc, yet no harmful effects have been observed.<sup>63</sup>

In his experience the author has been unable to trace any evil effect due to the presence of zinc in drinking water, even when the quantity rose as high as 23 p.p.m. in a water which is in constant use.

It might be well to add, that in the particular case just cited the zinc was derived from a long stretch of galvanized iron pipes and the amount of the metal present was subject to great and frequent fluctuations for reasons that were not apparent.

It must be admitted, however, that even on the assumption that the presence of zinc in a water is of no sanitary significance, its presence indicates serious deterioration of the piping system, and the probability of a proposed water supply being able to dissolve the metal should be determined and reported.

**Determination of Action of Water upon Metals.**—In reporting the possible action of water upon any of the common metals such action, whether of solution or erosion should be stated in parts per million, and it is convenient to standardize the conditions governing the action by allowing one liter of water to be in contact with one square decimeter of bright metal for one hour at 15° C.

The mode of procedure followed by the author is to submerge a piece of bright sheet metal, one decimeter square, in two liters of water contained in a wide-mouthed bottle. The water is occasionally given a gentle motion and is kept at 15 degrees for one hour, after which time the metal in solution or suspension is determined. One hour is sufficient time to allow of the watching of metallic solvency, and, let it be added, the limiting of the time of action to the standard period is important, for the rate of action of the same water is not only variable, but the ratio of the total action during different lengths of time is not a simple one. Thus, the quantity of metal attacked in ten hours is by no means ten times that acted upon during one hour.

Let it be said that although we know in a general way that softness, acidity, dissolved gases, and the presence of much chloride or nitrate will tend toward metallic solvency, while alkalinity and hardness are rated as protective agents, yet it is far better to actually test a water with reference to its behavior toward metals than to attempt any prophecy of its action based upon analytical knowledge of what the water may contain.

*Arsenic* occurs in some waters naturally, and both *arsenic* and *chromium* may be present from industrial waste. Should the presence of these elements be suspected, their determination should be undertaken, in the concentrated water, by the usual gravimetric methods.

## PHOSPHATES

Phosphates are rarely present in more than minute traces in waters fit for domestic use, although not uncommon in those which are contaminated. Excellent waters do at times contain them, however, in very notable quantities. For instance, the author found as much as two parts per million (calculated as calcium phosphate) in an artesian water on the New Jersey coast.

Hehner suggests .5 part of  $P_2O_5$  per million as the limit for good waters, but many excellent waters contain more than this amount.<sup>64</sup>

To determine them Phipson's method is convenient. He takes a large measure of the water, adds a little alum solution, followed by a few drops of ammonia, and then makes the solution acid with acetic acid. The aluminum phosphate is filtered off, dissolved in nitric acid, and precipitated with ammonium molybdate solution in the usual way.<sup>65</sup>

Woodman proposes a colorimetric method which takes but a short time.<sup>66</sup> Take 50 c.c. of the water. Add 3 c.c.  $HNO_3$ . Evaporate to dryness on the water bath. Heat for two hours in the water oven. Extract with cold water. Dilute to 50 c.c. in comparison tube. Add 4 c.c. ammonium molybdate (50 grams per liter) and 2 c.c.  $HNO_3$ . Mix, and after three minutes compare with standards prepared by diluting standard phosphate solution (.1 mg.  $P_2O_5$  per c.c.) to 50 c.c. and adding reagents as mentioned. A blank, using distilled water, should also be run.

#### MINERAL RESIDUE

Should a partial analysis of the mineral residue be demanded, which is not common except in the case of a "boiler" or a "mineral" water, one-half a liter, or more, of the water strongly acidulated with hydrochloric is evaporated nearly to dryness in platinum. When nearly dry acidify with  $HCl$  and complete the evaporation to dryness. The dry residue is heated in the air bath at  $120-130^\circ C$ . until acid fumes cease, then cooled, thoroughly moistened with hydrochloric acid, digested with water, filtered and washed.

The residue is dried, ignited, weighed, ignited with sulphuric and hydrofluoric acid and silica determined by difference in the usual manner.

<sup>64</sup> Thresh, op. cit.    <sup>65</sup> Chem. News, lvi, 251.

<sup>66</sup> J. Am. Chem. Soc., xxiv, 737.

*Barium*, if present, will be found in the residue after volatilizing the silicon fluoride.

It should be fused, brought into solution, and precipitated by sulphuric acid.

*Iron and Aluminum* are weighed together as oxides after oxidation and precipitation by ammonium hydroxide followed by ignition.

*Calcium* is thrown out of the filtrate from the iron and aluminum by ammonium oxalate as is usual and its filtrate is evaporated to dryness in platinum and ignited to remove excess of ammonium salts before precipitating *magnesium* in the customary manner.

*Lithium* is determined by Gooch's method given in J. Am. Chem. Soc., xii, 214.<sup>67</sup>

*Sulphates* are determined by use of barium chloride in a separate evaporation after removal of silica, iron and aluminum. For "boiler waters," however, Prof. Main suggests making the filtrate from the magnesium acid with hydrochloric acid and then precipitating at once with barium chloride. This saves much time and is convenient.

C. B. Dudley, formerly chief chemist of the Pennsylvania Railroad, determined scale-forming ingredients by determining the total solids as usual; treating the residue with 50 per cent alcohol and designating the undissolved material as "scale forming."

*Manganese* is determined by the following rapid method due to R. S. Weston.<sup>68</sup>

Take enough of the sample to give from .01 to 1 mg. of manganese. Evaporate with about 25 c.c. of nitric acid (1 acid to 3 water). Gently ignite the residue or bake it for one-half hour at 130° C. Add 50 c.c. of the nitric acid and when the solution is cool add about .5 gram of sodium bismuthate. Heat until the pink color disappears.

Add enough sodium thiosulphate to clear the solution

<sup>67</sup> Cf. Determination of Lithium, by Skinner and Collins, Bul. 153, Bureau of Chemistry, U. S. Dept. Agric.

<sup>68</sup> J. Am. Chem. Soc., xxix, 1074.

if manganese dioxide is precipitated, and heat to dispel all oxides of nitrogen. This step is usually unnecessary.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute (3 per cent) nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 c.c. with dilute nitric acid.

In another tube put 100 c.c. of dilute (3 per cent) sulphuric acid and add standard potassium permanganate solution until the color of the sample is matched. From the volume of potassium permanganate used calculate the weight of manganese.

The presence of chlorides interferes with the determination. Samples which contain large amounts of chloride should be treated before evaporation with a slight excess of silver nitrate and then filtered.

#### DISSOLVED OXYGEN

Dissolved oxygen may be determined by the Winkler method:

##### Reagents.

(a) *Manganous sulphate*.—Dissolve 480 grams of the salt in water and dilute the solution to 1 liter.

(b) *Alkaline potassium iodide*.—Dissolve 700 grams of potassium hydroxide or an equivalent amount of sodium hydroxide and 150 grams of potassium iodide in water and dilute the solution to 1 liter.

(c) *Starch solution*.—Mix a small amount of clean starch with cold water to form a thin paste and stir the mixture into 150 to 200 times its weight of boiling water. Boil for a few minutes, then sterilize. It may be preserved by adding a few drops of chloroform.

**Standard Sodium Thiosulphate. 0.025N Solution.**—Dissolve 6.205 grams of chemically pure recrystallized sodium thiosulphate in water and dilute the solution to 1 liter with freshly boiled and cooled distilled water. Each cubic centimeter is equivalent to 0.2 mg. of oxygen or to

0.1395 c.c. of oxygen at 0° C. and 760 m.m. pressure. Inasmuch as this solution is not permanent it should be standardized occasionally against a 0.025N solution of potassium dichromate.

**Collection of Sample.**—Collect the sample in a narrow-necked glass-stoppered bottle of 250 to 270-c.c. capacity. The following procedure should be followed in order to avoid entrainment of absorption of atmospheric oxygen. In collecting from a tap fill the bottle through a glass or rubber tube extending well into the tap and to the bottom of the bottle. To avoid air bubbles allow the bottle to overflow for several minutes, and then carefully replace the glass stopper so that no air bubble is entrained. In collecting from a pond or tank connect the sample bottle to a bottle of a liter capacity. Provide each bottle with a two-hole rubber stopper having one glass tube extending to the bottom and another glass tube entering but not projecting into the bottle. Connect the short tube of the sample with the long tube of the liter bottle. Immerse the sample bottle in the water and apply suction to the outlet of the liter bottle. To collect a sample at any depth arrange the two bottles so that the outlet tube of the liter bottle is at a higher elevation than the inlet tube of the sample bottle. Lower the two bottles in any convenient form of cage, properly weighted, to the desired depth. Water entering during the descent will be flushed through into the liter bottle. When air bubbles cease rising to the surface, raise the bottle. Finally replace the perforated stopper in such a manner as to avoid entraining bubbles of air.

**Procedure.**—Remove the stopper from the bottle and add 1 c.c. of the manganous sulphate solution and 3 c.c. of the alkaline potassium iodide solution. Allow the precipitate to settle. Add 1 c.c. of the concentrated sulphuric acid and mix by shaking.

The procedure to this point must be carried out in the field, but after the acid has been added and the stopper



replaced there is no further change, and the rest of the test may be performed within a few hours, as convenient. Transfer 200 c.c. of the contents of the bottle to a flask and titrate with 0.025N sodium thiosulphate, using a few cubic centimeters of the starch solution as indicator toward the end of the titration. Do not add the starch solution until the color has become faint yellow. Titrate until the blue color disappears. If 200 c.c. of the sample are taken the number of cubic centimeters of 0.025N thiosulphate used is equal to parts per million of oxygen. Correction for volume of reagents added amounts to less than 3 per cent and are not justified except in work of unusual precision. To obtain the result in cubic centimeters per liter multiply the number of cubic centimeters of thiosulphate used by .698.

After a careful study of various methods for the determination of dissolved oxygen, Theriault (U. S. Public Health Bull. 151, p. 37) concluded that:

"In the absence of organic matter, nitrites and iron salts, Winkler's original procedure is subject to relatively few sources of error. In order to assure the complete absorption of the dissolved oxygen it is desirable, however, after the precipitated manganese hydroxides have partially settled out, again to mix the contents of the bottle and allow the precipitate to settle a second time.

A measurable loss of iodine occurs when the usual titrimetric procedure is followed of measuring out a definite volume of the iodine solution into a separate container. This loss, however, is small and it may be entirely eliminated by conducting the titration in the sample bottle itself. The data submitted also indicate that, if necessary, this slight error might be reduced to a negligible value by the use of larger amounts of iodide.

While the precision of the unmodified Winkler method is of a high order, its practical application is restricted to relatively pure waters. The various modifications applicable to samples containing appreciable amounts of organic matter, nitrites and iron salts are to be used with caution. In the stream-pollution investigations conducted by the United States Public Health

Service, the Rideal-Stewart (permanganate) modification has been adopted."

The following method is that devised by M. Albert-Levy, of the Montsouris Observatory, Paris, and is now rarely used except in the presence of iron salts.

A pipette of about 200-c.c. capacity is provided with an upper and lower stopcock, the bore of the upper one being large, and the true capacity between the stopcocks is determined. Above the upper stopcock the tube is expanded into a short cylindrical funnel. The pipette is completely filled with water to be examined, and the funnel is emptied. The cocks having been closed, the pipette is wiped off and fixed in a suitable clamp. Two c.c. of dilute potassium hydroxide solution are placed in the funnel and, by careful opening of the cocks, introduced within the pipette without the admission of air. After washing the funnel 4 c.c. of a solution of ammonium ferrous sulphate are placed therein, and, by similar means, also admitted with the pipette. In presence of the alkaline solution the oxygen dissolved in the water will in five minutes, after gentle agitation, oxidize the ferrous salt to ferric, and a mixture of the two hydroxides will shortly settle to the bottom. After again washing the funnel 2 c.c. of concentrated sulphuric acid are placed therein, and the upper stopcock alone is opened. The higher gravity of the acid will cause it to slowly enter the pipette, where it will acidify the contents and dissolve the hydroxides of iron. The contents and washings of the pipette are turned into a flask and titrated with the standard solution <sup>69</sup> of potassium

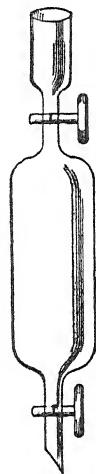


FIG. 11.—Oxygen Sampler.

<sup>69</sup> Should much chloride be present, as in sea water, M. Albert-Levy suggests the substitution of the bichromate in place of the permanganate of potassium.

permanganate described on p. 78. A blank is now titrated containing a mixture of a pipetteful of the water, 2 c.c. of the sulphuric acid, 2 c.c. of the potassium hydroxide solution, and 4 c.c. of the ammonium ferrous sulphate solution. The difference between these two titrations (acid reaction having prevented oxidation in the second instance) will give the amount of ferrous salt oxidized by the oxygen dissolved in the water. The volume of the water operated upon will be the volume of the pipette ( $V$ ) less the volumes of the alkaline and iron solutions, namely:

$$V - (2+4) \text{ c.c.}$$

Report the dissolved oxygen as parts per million by weight, and report it also after noting the temperature of the water, as a percentage of the oxygen required for complete saturation at the observed temperature, making use of the following table:

VOLUME OF OXYGEN, IN CUBIC CENTIMETERS, REQUIRED TO SATURATE ONE LITER OF WATER AT VARIOUS DEGREES CENTIGRADE. (WINKLER.) \*

Degree.	C.C.	Degree.	C.C.	Degree.	C.C.
0	10.187	11	7.692	21	6.233
1	9.910	12	7.518	22	6.114
2	9.643	13	7.352	23	5.999
3	9.387	14	7.192	24	5.886
4	9.142	15	7.038	25	5.776
5	8.907	16	6.891	26	5.669
6	8.682	17	6.750	27	5.564
7	8.467	18	6.614	28	5.460
8	8.260	19	6.482	29	5.357
9	8.063	20	6.356	30	5.255
10	7.873				

\* Berichte, 22, 1889, 1772.

Palmer points out that supersaturation of water with oxygen may be caused by the liberation of the gas through the action of either microorganisms or larger plants containing chlorophyl.<sup>70</sup>

Deep samples for dissolved oxygen are taken by attach-

<sup>70</sup> Streams Examination, p. 87

ing to the lower end of the pipette a short rubber tube, which may be flexed upon itself by pulling a string fastened to its extremity.

The pipette having been sunk with the rubber tube closed by flexion and with both cocks open, water is admitted by allowing the string to slacken. The string is again tightened and the pipette raised toward the surface. The cocks should be carefully closed before the surface is fully reached. It is still better to sink two pipettes connected together in tandem and to use the water collected by the lower one.

*Carbon dioxide* in solution tends to cause a solvent action upon metals, especially if the water be soft.

Should it be decided to include an estimation of carbon dioxide in the analysis, take 100 c.c. of the water and titrate with standard  $\text{Na}_2\text{CO}_3$  solution, using phenolphthalein as an indicator.<sup>71</sup>

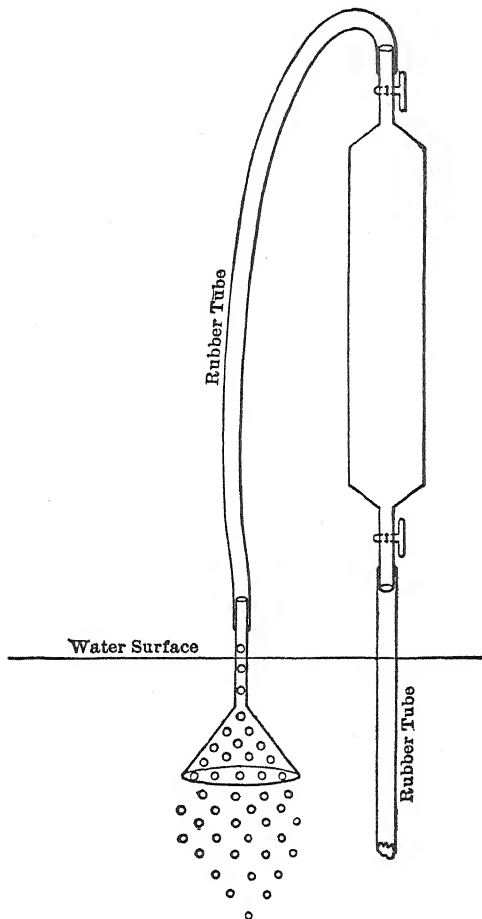


FIG. 12.—Sampler for Gases.

<sup>71</sup> Chem. News, lxx, 104.

The determination of other gases present in solution is not commonly of sufficient value to repay the expenditure of time required for such work.

Of course, determination of  $H_2S$  is important when dealing with mineral waters of the "sulphur" group.

An odor like that of sulphuretted hydrogen must not be taken as proof positive of the presence of that gas in a water, inasmuch as mixtures of sundry hydrocarbons will often greatly mislead the sense of smell.

Samples in which dissolved gases are to be determined should be examined in the field. They do not admit of transportation.

When it is desired to secure for analysis a sample of the gas that sometimes is observed to bubble in considerable volume from certain springs, the device illustrated on p. 99 will be found of value. The whole apparatus having been filled with water and then placed in the position indicated, the gas will be sucked over into the sampling cylinder upon opening the stopcocks. The stopcocks are then closed and the sample is ready for shipment.<sup>72</sup>

#### DETERMINATION OF FREE CHLORINE <sup>73</sup>

The orthotolidine test for the quantitative determination of minute quantities of free chlorine and hypochlorites in waters, was first proposed by Phelps in 1909. Since that time it has enjoyed considerable study and wide usage. This colorimetric test depends on the amount of the reagent that is affected by the residual chlorine. The test is not specific, for it gives similar reactions with other oxidizing and certain reducing agents.

##### Reagents.

(a) *Orthotolidine Reagent*.—Dissolve 1.0 gram of pulverized C. P. o-tolidine, m.p. 125° C., in one liter of dilute hydrochloric acid (100 c.c. conc. HCl diluted to one liter).

<sup>72</sup> Travers, Study of Gases, p. 44.

<sup>73</sup> Prepared by Dr. C. S. Boruff.

If the pure, light brown, reagent is used and is pulverized before being added to the dilute acid, the reagent goes into solution immediately. The C. P. o-tolidine, product No. 249, prepared by Eastman Kodak Co., Rochester, N. Y., has been found very satisfactory.

(b) *Copper Sulphate Solution for Standards*.—Dissolve 1.5 grams of copper sulphate crystals,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and 1.0 c.c. of concentrated sulphuric acid in distilled water and dilute to 100 c.c.

(c) *Potassium Dichromate Solution for Standards*.—Dissolve .025 gram of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and 0.1 c.c. of concentrated sulphuric acid in distilled water and dilute to 100 c.c.

**Procedure**.—Thoroughly mix 1 c.c. of the o-tolidine reagent with 100 c.c. of the water to be tested in a 100-c.c. Nessler tube of the same dimensions as those used in preparing the standards. Let stand five minutes and then compare the color developed with that of the standards which have been prepared in accordance with the table in the Appendix. The standard tubes read in parts per million of free chlorine.

#### NOTES

Low readings are obtained if cold waters (less than  $15^\circ \text{C}$ .) are tested as outlined. (2)

Ferric iron, manganese (other than the bivalent ion) and other oxidizing agents, as well as high concentrations of nitrites (2.0 to 6.0 p.p.m. as nitrite nitrogen) increase the depth of color and hence interfere with the test. (2, 3, 5)

For highly buffered waters or solutions a reagent containing more acid is advisable. (1, 6)

For turbid or colored waters, or waters containing interfering quantities of manganese, iron or nitrites, a block comparator or an outfit such as the La Motte-Enslow Chlorine Comparator is advisable. (4)

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## CHAPTER III

### ROUTINE LABORATORY METHODS FOR THE ESTIMATION OF MINERAL CONSTITUENTS

It has been our observation that students do not experience much difficulty in mastering the technique of individual chemical tests. But the organization of a series of tests into a sequence which will be sound from a chemical standpoint, and in which the errors are consistent with the degree of accuracy actually necessary, and which will give the required results with a minimum of calculation, is quite a different matter.

Such aids as Dr. Chandler's "assay ton" system of weights or the choice of standard solutions to read in parts per million direct from the burette instead of choosing solutions with a simple normality factor should be thoroughly investigated by the chemical analyst. The author knows of no better material for the study of these "tricks of the trade" than is water analysis.

There are three rather distinct fields requiring information concerning the saline or mineral content of water, and three series of tests have come into use to serve these tests.

The first is the routine or daily control of the chemicals required for water softening. The water to be tested has usually been under observation for some time, its variations are known in a general way, and speed and simplicity are important. These requirements are admirably served by the methods adopted by the A. R. E. A. and reprinted here by permission. It will be noted that the burette reads in grains per gallon. How may the volume of sample used

in each test be varied so that the results will read in  $\frac{\text{p.p.m.}}{10}$ ?



STANDARD METHODS OF WATER ANALYSIS AND INTERPRETATION  
OF RESULTS<sup>1</sup>

**General.**—The general practice for reporting water analyses is in terms of grains per United States gallon, which is equivalent to parts per 58,341. This appears to convey a better impression of the actual condition of the water, which is the ultimate purpose of the analysis, and it is recommended that reports of water analysis in grains per gallon with supplementary advice as to pounds per thousand gallons of total incrustants, total non-incrustants, and total solids, be adopted as standard practice.

**Form and Combination.**—Although the actual determination of substances in water are usually made of the various elements or radicals direct, the customary and accepted practice for reporting results of water analysis is by hypothetical combinations of the elements. The following method is recommended for uniformity:

**Silica—as found.**—Iron and aluminum oxides—as found (except in special cases of acidity, where more extensive determination should be made). Make combination of positive radical determined, to negative radicals as found, in following order of sequence:

## Positive Radicals

Calcium  
Magnesium  
Sodium  
Potassium

## Negative Radicals

Carbonate  
Sulphate  
Chloride  
Nitrate

**Interpretation.**—*Incrustants.*—It is understood that the silica, iron and aluminum oxides, and the calcium and magnesium combinations will be classed as incrusting solids.

*Nonincrustants.*—The sodium, alkali salt combinations, and organic matter will be classed as nonincrusting.

*Corrosive.*—All acids, iron and aluminum sulphate, calcium chloride and nitrates, magnesium sulphate (in appreciable amounts), chloride, and nitrate will be classed as corrosive salts.

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## METHOD OF ANALYSIS

**Field Survey or Rapid Check Tests.**—Field survey tests for boiler waters are generally confined to a means of approximating the total hardness or total amount of scale forming matter, and the division of this figure into the alkalinity (carbonate hardness) and the sulphate hardness, as well as an approximation of the ratio of the calcium and magnesium salts. With experience in manipulation, the following procedure can be made to give close and very satisfactory results.

**Reagents.**—1. *Standard Calcium Chloride Solution.*—Dissolve .5 gram of pure calcite (calcium carbonate) in a little dilute hydrochloric acid, being careful to avoid splattering. Wash down and neutralize with ammonium hydroxide to slight alkalinity, litmus paper indicator. Make up to 500 c.c. with carbon dioxide free distilled water and store in glass-stoppered bottle. One cubic centimeter of this solution is equivalent to one milligram calcium carbonate.

2. *Standard Soap Solution.*—Make up stock solution by shaking vigorously, approximately 100 grams of powdered castile soap or sodium oleate in one liter of 80 per cent grain alcohol or nearest obtainable equivalent denatured with methyl alcohol and allow to stand at least overnight. Dilute the clear supernatant liquid with 70 per cent grain alcohol or nearest obtainable equivalent denatured with methyl alcohol, until one cubic centimeter is equivalent to one cubic centimeter of the standard calcium chloride solution, making due and recorded allowance for a lather factor which will vary from .7 to 1.4 c.c. with different soaps. One cubic centimeter of this solution is equivalent to one milligram calcium carbonate.

3. N/50 sulphuric acid.

4. N/50 sodium carbonate.

**Procedure**—(a) Measure 58.3 c.c. of the water into an eight-ounce bottle. Add the standard soap solution one cubic centimeter at a time, shaking vigorously after each addition, until a strong permanent lather is secured, and as the end point is approached, cut the additions of soap solution to .5 c.c. Make note of the false end point, which is the dividing line between the calcium and magnesium salts and record. The final end point, after deducting lather factor, gives direct the

total hardness as grains per gallon in terms of calcium carbonate. The difference between the false point and the total hardness gives the amount of magnesium salts, the balance being calcium salts, all as grains per gallon in terms of calcium carbonate. In determining the hardness in acid waters, they should first be rendered neutral to methyl orange by addition of N/50 sodium carbonate. If hardness test runs above 15.0, it is best to take aliquot portion and dilute to 58.3 c.c. with distilled water, so that the later end point will be less than 15, multiplying the result accordingly to obtain correct hardness.

(b) Titrate 58.3 c.c. of the water with N/50 sulphuric acid solution methyl orange indicator, and record as alkalinity, this point being the carbonate hardness in terms of calcium carbonate direct as grains per gallon.

In case of alkaline waters, if the total hardness is greater than the alkalinity, the difference between the two represents sulphate hardness. If the total hardness is less than the alkalinity, the difference is sodium carbonate, all of the hardness being carbonate hardness, the hardness being composed in either case of calcium or magnesium salts as determined by the false and true end points in the soap test. In case of acid waters, all the hardness will be sulphate hardness.

(c) In case the water is acid to methyl orange, titrate 58.3 c.c. with N/50 sodium carbonate solution and record acidity direct as grains per gallon in terms of calcium carbonate.

(d) When treated water is being tested, first titrate 58.3 c.c. of the water with N/50 sulphuric acid, phenolphthalein indicator. Double the reading and report as causticity. Continue the titration with methyl orange indicator, recording the reading direct as alkalinity. Soap test is made as noted and reported as hardness.

The difference between the hardness and alkalinity shows an overtreatment in soda ash if the alkalinity is in excess, or an undertreatment if the hardness is in excess, directly in grains per gallon in terms of calcium carbonate. Likewise, the excess of causticity over alkalinity indicates an overtreatment with lime or caustic soda, while an excess of alkalinity over causticity shows an undertreatment direct in grains per gallon in terms of calcium carbonate. In other words, this difference shows the excess or deficiency of hydrate alkalinity.

**Rapid Laboratory Method.**—This method is recommended for routine laboratory procedure where quick results are desired which will satisfactorily differentiate between constituents normally present in waters, and furnish sufficient information for making an ordinary analysis report, so that judgment may be made as to general effect of quality.

**Reagents.**—(a) Standard soap solution, 1.0 c.c. equivalent to 1.0 mg. calcium carbonate.

(b) N/50 sulphuric acid.

(c) N/20 soda reagent, prepared of one-half N/20 sodium hydroxide and one-half N/20 sodium carbonate.

(d) Clear saturated lime water, prepared by shaking excess of C. P. hydrated lime with distilled water and let settle.

(e) Standard sodium chloride solution, 1.0 gram dissolved in 1000 c.c. distilled water. One cubic centimeter is equivalent to 1.0 mg. NaCl.

(f) Standard silver nitrate solution. One cubic centimeter is equivalent to 1.0 c.c. standard sodium chloride solution.

**Procedure**—(a) Evaporate 58.3 c.c. of water to dryness in weighed dish, and bake for thirty minutes at 180° C. Weigh up as total solids, milligrams, giving grains per gallon direct.

(b) Titrate 58.3 c.c. of the water with N/50 sulphuric acid, and methyl orange indicator, which gives grains per gallon of carbonate and hydrate alkalinity direct from number of cubic centimeters used, in terms of calcium carbonate.

(c) Take 116.7 c.c. of water in 250-c.c. Erlenmeyer flask and boil for fifteen minutes. Add predetermined amount of soda reagent from pipette, so that, as shown by soap test, there will be an excess equivalent to at least ten grains per gallon. Boil ten minutes additional and then pour into 200-c.c. graduated flask, adding sufficient distilled water so that solution will be at mark, then cool. Filter off 100 c.c. and titrate with N/50 sulphuric acid, methyl orange indicator. Along with this sample a blank should be run using the same amount of distilled water as in sample and treated with same amount of soda reagents, making up to 200 c.c. after boiling. The difference between amount N/50 sulphuric acid required for neutralizing 100 c.c. of blank and the sample gives the incrusting sulphates direct in terms of calcium carbonate. If the difference is negative,

it shows the amount of free sodium carbonate direct as grains per gallon in terms of calcium carbonate.

(d) Take 116.7 c.c. of samples in 250-c.c. Erlenmeyer flask and exactly neutralize, methyl orange indicator. Boil fifteen minutes to expel all carbon dioxide and then add solution of saturated lime water so that, as shown by soap test, there will be an excess equivalent to at least ten grains per gallon. Continue boiling for fifteen minutes. Pour into 200-c.c. graduated flask and add distilled water so that solution will be at mark when cool. Filter and titrate 100 c.c. with N/50 sulphuric acid. Along with this sample a blank should be run using the same amount of distilled water as in sample and treated with the same amount of saturated lime water, making up to 200 c.c. after boiling. The difference between amount of N/50 sulphuric acid required for neutralizing 100 c.c. of blank and the sample gives the amount of magnesium present direct in grains per gallon in terms of calcium carbonate.

(e) In making final report compare results from (c) and (d). If (c) is in excess of (d), calculate (d) direct to magnesium sulphate and the difference to calcium sulphate, all of (b) being calcium carbonate.

If (c) is less than (d) calculate (c) direct to magnesium sulphate and the remainder of (d) to magnesium carbonate, this remainder of (d) being also subtracted from (b) the difference being calcium carbonate. If (c) is negative, make proper allowance in (b) for the amount of sodium carbonate, calculate (d) to magnesium carbonate, making allowances in (b) and the remainder of (b) being calcium carbonate.

(f) Titrate 58.3 c.c. sample with silver nitrate solution, potassium chromate indicator. Result gives sodium chloride direct in grains per gallon.

(g) If the silica and iron aluminum content amount to more than one grain per gallon, it may be well to separate and weigh up by the usual gravimetric methods, using 291-c.c. sample and multiplying diagrams by 2 to obtain grains per gallon. If the amount is below this, which is usually the case, it can be estimated with sufficient accuracy by colorimetric determination.

(h) The difference between (a) and the sum of calculations in (e), (f) and (g) gives the amount of nonincrusting sulphates, nitrates and organic matter. There is no necessity for separat-

ing these constituents in the ordinary boiler-water analysis unless, after heating the residue in the (a), a black discoloration shows high organic matter which might induce foaming. The sulphate may then be determined gravimetrically as barium sulphate or rapidly by the Parr sulphotometer, and the organic matter taken as the difference.

**Full and Complete Laboratory Examination.**—For full and complete examination of boiler waters as may be required in special cases, it is recommended that the procedure outlined in the latest edition of Standard Methods of Water Analysis, published by the American Public Health Association, 370 Seventh Avenue, New York, be followed. These methods were adopted as standard by that association after collaboration with other scientific societies, and have been universally accepted.

It is sometimes advantageous for field use, especially in the control of zeolite water softeners, to employ a soap solution of greater strength than the one specified. For this purpose the solution described by Bountron and Boudet<sup>2</sup> is suggested. The preparation of this solution and its use is described as follows:

Dissolve 100 grams of pure soap in 1600 c.c. of 90 per cent grain alcohol. Dilute with distilled water (800 to 1000 c.c. will be required) until 2.4 c.c. of the soap solution gives a lather with 40 c.c. of a solution of  $\text{CaCl}_2$  containing .25 gram per liter. The  $\text{CaCl}_2$  solution may be made up by dissolving 0.225 gram of pure  $\text{CaCO}_3$ , using the technique described (see Standard Soap) and diluting to one liter.

This soap solution is approximately three and one-half times as strong as the Standard Soap previously described, and is to be used for field determinations of "zero hardness." For this purpose 40 c.c. of the water to be tested are placed in a three-ounce cork-stoppered bottle and the soap solution added a drop at a time from any convenient type of dropping bottle which delivers .05 c.c. per drop.

<sup>2</sup> Comptes Rend. 40, 1844, p. 679, translated by A. M. Buswell, American Water Works Association Journal, 9, 892 (1922).

The sample is shaken vigorously after each addition of soap. Three drops should give a permanent lather with 40 c.c. of distilled water or water of "zero hardness."

### BOILER-WATER ANALYSIS

For many years the Illinois State Water Survey has found that an abbreviated mineral analysis of the residue furnishes all the information necessary for judging the suitability of a water for a large variety of purposes. In laboratory slang this has come to be called a "boiler analysis," since it is applied to waters used for steam boilers more frequently than to any others. In this system less care is taken in the separation of calcium and magnesium, and the determination of potassium is dispensed with.

In the Boiler-Water Analysis, as made in this laboratory, the following determinations are made:

Residue on evaporation	Ammonia
Iron	Sulphate
Manganese	Nitrate
Silica	Chloride
Calcium	Alkalinity
Magnesium	

These determinations are described in the order given:

#### RESIDUE ON EVAPORATION—GRAVIMETRIC

**Procedure.**—This determination is made as directed in Standard Methods of Water Analysis, sixth edition, 1925 p. 25, except that a pyrex glass dish is substituted for the platinum dish. The dish is cleaned, dried at 180° C. for an hour, cooled in a desiccator, and weighed. Into this are then measured 100 c.c. of the water and this sample is evaporated to dryness on the steam bath. It is then dried at 180° C. for an hour, cooled in a desiccator, and weighed. The difference in weight between this and the empty dish expressed in milligrams multiplied by 10 gives parts per million of residue on evaporation.

## IRON—COLORIMETRIC

**Reagents.**

Hydrochloric Acid—Conc.

Potassium Permanganate—6.30 grams made up to a liter with distilled water.

Potassium Thiocyanate—20 grams per liter.

*Standards.*—1. Standard ferric solution (Standard Methods of Water Analysis, p. 46): Dissolve .70 gram of crystallized ferrous ammonium sulphate in 50 c.c. distilled water and 20 c.c. of dilute sulphuric acid. Warm the solution and add potassium permanganate until the iron is completely oxidized. Dilute one liter: 1 c.c. contains 0.1 mg. Fe.

2. Permanent standards may be made using solutions of potassium chloroplatinate and cobaltous chloride. Directions for making these standards are given in Appendix I. These permanent standards as described check the standard iron colors in the low range very well but do not check so closely in the higher range. If the low form tube is used the check is better.

**Procedure.**—Fifty cubic centimeters of the sample of water are measured into a 50-c.c. Nessler tube and one cubic centimeter of concentrated HCl and three drops of the potassium permanganate solution are added. The mixture is shaken and allowed to stand for ten minutes. At the end of this time 5 c.c. of the potassium thiocyanate solution are added, the contents of the tube well mixed and the resulting brownish red color compared with that of appropriate standards prepared from the standard ferric solution in exactly the same way. An appropriate series of standards is made by measuring into 50-c.c. Nessler tubes .1, .3, .5, .7, and 1.0-c.c. portions of the standard iron solution. These are all made up to 50 c.c. and treated exactly the same as the unknown. The number of cubic centimeters of standard matching the unknown multiplied by 2 gives parts per million of iron (Fe). That



is, if 50 c.c. of the unknown gives a color which matches the standard in which there are .3 c.c. of standard, then the unknown contains .6 p.p.m. of iron.

### MANGANESE—COLORIMETRIC

#### Reagents.

Nitric Acid—Conc.

Silver Nitrate—20 grams per liter.

Ammonium Persulphate—solid.

Sulphuric Acid—Conc.

*Standards.*—Standard manganous sulphate. (Standard Methods of Water Analysis, p. 50): Dissolve .2873 gram of purest potassium permanganate in about 100 c.c. of distilled water. Acidify the solution with sulphuric acid and heat to boiling. Add slowly a sufficient quantity of dilute solution of oxalic acid to discharge the color. Cool and dilute to one liter: 1 c.c. of this solution contains .1 mg. of Manganese.

*Procedure.*—One hundred cubic centimeters of the sample are measured into a 250-c.c. beaker. If chloride is low, 1 c.c. of nitric acid is added and the sample heated almost to boiling. Silver nitrate solution is added so that there will be 1 c.c. in excess of the precipitated silver chloride. About .5 gram of ammonium persulphate is added and almost immediately the pink color of permanganate is obtained if manganese is present. This color is compared with appropriate standards which are made up by diluting .2, .4, .6, .8 c.c., etc., portions of the standard manganese solution to 100 c.c. and treating exactly as the unknown. Using a 100-c.c. sample of water the standards read directly in parts per million. That is, if the color of the unknown matches that of the standard in which is present .6 c.c. of the standard manganese solution the water contains .6 p.p.m. of Mn.

If chloride is high (100 p.p.m. or more), the sample is first evaporated to white fumes with 5 c.c. of concentrated sulphuric acid. It is then cooled, diluted to 100 c.c. with

distilled water, 1 c.c. concentrated nitric acid added and treated as before.

## SILICA—COLORIMETRIC

**Reagents.**

Ammonium Molybdate Reagent—30 grams ammonium molybdate.

200 c.c. of 1 : 1 HCl.

400 c.c. of distilled water.

*Standards.*—530 gram  $K_2CrO_4$  in 100 c.c. water. One cubic centimeter of this solution diluted to 55 c.c. in a Nessler tube gives a color which is equivalent to that developed when 1 mg. of  $SiO_2$  in a 50-c.c. volume reacts with 5 c.c. of the molybdate solution (making a total volume of 55 c.c.). Or using a 50-c.c. sample for the determination, 1 c.c. of the chromate solution is equivalent to 20 p.p.m.  $SiO_2$ . Permanent standards reading directly in parts per million when a 50-c.c. sample is used, may be made as follows:

c.c. Chromate Dil. to 55 c.c.	Equivalence in P.P.M. $SiO_2$ when 50-c.c. Sample is Used.	c.c. Chromate Dil. to 55 c.c.	Equivalence in P.P.M. $SiO_2$ when 50-c.c. Sample is Used.
0.0	0	0.8	16
.1	2	.9	18
.2	4	1.0	20
.3	6	1.1	22
.4	8	1.2	24
.5	10	1.3	26
.6	12	1.4	28
.7	14	1.5	30

**Procedure.**—Fifty cubic centimeters of the sample are measured into a tall form Nessler tube. Five cubic centimeters of the molybdate reagent are added, the mixture thoroughly shaken, and allowed to stand about fifteen minutes—not longer than twenty minutes. The yellow color developed is then compared with the chromate

standards which are made to read directly in parts per million.

### CALCIUM—GRAVIMETRIC

#### Reagents.

Hydrochloric Acid—Conc.

Ammonium Hydroxide—Conc.

Ammonium Oxalate Solution—Saturated.

Wash Water—Dilute saturated solution of ammonium oxalate 1 to 5 and add a little  $\text{NH}_4\text{OH}$ . This gives an approximate 1 per cent solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

**Procedure.**—Into a 400-c.c. beaker are measured 200 c.c. of the sample of water. To this are added 10 c.c. of concentrated  $\text{HCl}$  and the sample is evaporated to about 100 c.c. (the large excess of  $\text{HCl}$  is added so that  $\text{NH}_4\text{Cl}$  will be formed upon subsequent addition of  $\text{NH}_4\text{OH}$  in such quantity as to prevent the precipitation of  $\text{Mg}(\text{OH})_2$ ). The sample is made alkaline to methyl red with  $\text{NH}_4\text{OH}$  and the calcium precipitated hot with ammonium oxalate. About 5 c.c. of this solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  is usually sufficient. The mixture is digested just below boiling until the precipitate has completely settled out. The calcium oxalate is then filtered off on quantitative paper, washed with the hot oxalate wash solution, dried and ignited in a platinum crucible which has previously been ignited, cooled, and weighed. (The filtrate is saved for magnesium determination.) The weight in milligrams of  $\text{CaO}$  multiplied by 3.5715 gives parts per million of  $\text{Ca}$ .

### CALCIUM—VOLUMETRIC (OPTIONAL)

#### Reagents.

Hydrochloric Acid—Conc.

Ammonium Hydroxide—Conc.

Ammonium Oxalate Solution—Saturated.

Sulphuric Acid—6N(1 : 6).

Potassium Permanganate—Standard (about N/5).

**Procedure.**—The procedure for this determination is the same as that for the gravimetric determination up to the precipitation of the calcium as the oxalate. A 200-c.c. sample of water is made acid with 10 c.c. of hydrochloric acid, evaporated to about 100 c.c. volume, then made alkaline to methyl red with ammonia and the calcium precipitated with ammonium oxalate solution. Instead of filtering off the precipitate and igniting as in the gravimetric determination, it is filtered off, washed with hot water, dissolved in hot sulphuric acid (1 : 6), made up to about 200 c.c. volume, and the oxalic acid titrated hot with the standard permanganate solution. The number of cubic centimeters of permanganate necessary for this titration, multiplied by a factor determined by the strength of the permanganate, gives the amount of calcium present.

The permanganate is standardized by titrating it against a definite volume of standard sodium oxalate solution. This titration is carried out the same as is that of the unknown.

The precipitated calcium oxalate may be filtered off on filter paper which is then transferred with the precipitate to a beaker and hot sulphuric acid added. It has been found that a more rapid procedure is the use of a glass crucible with a sinter glass bottom. By using this crucible suction can be brought into play and the filtration speeded up considerably. (A glass crucible of porosity 3 has been found most satisfactory.) The precipitate is filtered out in the crucible, washed with hot water, dissolved in hot acid and titrated with the standard permanganate solution.

#### MAGNESIUM—GRAVIMETRIC

##### Reagents.

Sodium Ammonium Hydrogen Phosphate (microcosmic salt)—Saturated solution.

Ammonium Hydroxide—Conc.

Wash Water { 12 c.c.  $\text{HNO}_3$ —Conc.  
                  { 73 c.c.  $\text{NH}_4\text{OH}$ —Conc.

415 c.c.—Dist.  $\text{H}_2\text{O}$ .

**Procedure.**—The filtrate plus washings from the calcium determination (which together should have a volume of 150–200 c.c.) is used for the determination of magnesium. Twenty cubic centimeters of the saturated microcosmic-salt solution are added to the sample and concentrated ammonium hydroxide is added with constant stirring until the mixture gives a blue color with thymol blue. The mixture is allowed to stand for at least six hours, preferably overnight. The precipitated magnesium ammonium phosphate is then filtered off on a weighed Gooch crucible, washed two or three times with the wash water described, ignited to pyrophosphate and weighed. The weight of  $Mg_2P_2O_7$  in milligrams multiplied by 1.092 gives parts per million of magnesium.

#### AMMONIA—COLORIMETRIC

Ammonia nitrogen is determined as described, pp. 61–62. In the report of the Boiler-Water Analysis this is reported as the ammonium ion ( $NH_4^+$ ). The value for ammonia nitrogen multiplied by 1.288 gives ( $NH_4^+$ ).

#### SULPHATE—GRAVIMETRIC

##### Reagents.

Barium Chloride Solution—10 per cent.

Hydrochloric Acid—Conc.

**Procedure.**—Into a 400-c.c. beaker are measured 200 c.c. of the sample of water. This sample is made acid to methyl red indicator with HCl and about a half cubic centimeter excess is added, after which the sample is concentrated by evaporation to about 100 c.c. Precipitation of the sulphate is made (hot) by adding with stirring about 5 c.c. of the 10 per cent  $BaCl_2$  solution. If the sulphate is high, it may necessitate the use of more of the precipitant. The mixture is heated just below boiling until the precipitated  $BaSO_4$  has completely settled out, when it is filtered on a weighed Gooch crucible washed with

hot water, ignited and weighed as  $\text{BaSO}_4$ . The weight of  $\text{BaSO}_4$  in milligrams multiplied by 2.0575 gives parts per million of sulphate ion.

#### NITRATE—COLORIMETRIC

Nitrate nitrogen is determined as outlined on pp. 53-54. The value for nitrate nitrogen multiplied by 4.426 gives nitrate ( $\text{NO}_3^-$ ), which is reported in the Boiler-Water Analysis.

#### CHLORIDE—VOLUMETRIC

Chloride is determined as outlined on pp. 45-46, and is reported as such.

In case the chloride ion is very high, say above 200 p.p.m., the method for its determination as outlined is not reliable. In such a case an appropriate sample of the water is treated with about one cubic centimeter of concentrated nitric acid, heated almost to boiling, and an excess of standard silver nitrate is added. The precipitate of silver chloride is caused to settle by heating and stirring. When the liquor is perfectly clear above the precipitate, it is allowed to cool and the excess silver nitrate determined by titration with standard potassium thiocyanate, using one cubic centimeter of ferric alum solution as an indicator (this is the Volhard method for chloride).

To determine the size sample of water on which to make this determination, it is best to determine an approximate chloride value. This may be done by using approximate solutions of  $\text{AgNO}_3$  and  $\text{KCNS}$ . After this determination is made, consultation of the table on the next page will give the correct sample to be used for the more careful determination.

In samples which are high in chloride it has been found that the value for the chloride ion is quite generally approximately half the value for total residue. This is the case so consistently that it has been used with good success in place of the approximate chloride determination in deciding the size of the sample for analysis.

Approximate Chloride	Dilution, c.c.	For Analysis, Take c.c.	Factor
up to 1,600	none	50	20
1,700 to 3,200	none	25	40
3,300 to 8,000	100 to 500	50	100
9,000 to 16,000	50 to 500	50	200
17,000 to 32,000	50 to 1000	50	400
33,000 to 64,000	50 to 1000	25	800
65,000 to 120,000	50 to 1000	25*	800

\* Use 50 c.c.  $\text{AgNO}_3$ , for this. In all others use 25 c.c.

### ALKALINITY—VOLUMETRIC

Alkalinity is determined as outlined on pp. 13-14, and reported as parts per million in terms of  $\text{CaCO}_3$ .

### SODIUM CALCULATION

Upon completion of these determinations the positive ion values expressed as milliequivalents are summed up, also the negative milliequivalents. The sum of the negative milliequivalents minus the sum of the positive milliequivalents, gives a value which is reported as milliequivalents of sodium. In some cases the positives are higher than the negatives thus showing no sodium present. In such cases the inclusion of silica as the negative silicate ion increases the sum of the negatives above that of the positives. This will then show the presence of sodium.

Other determinations are usually made on these samples, such as color, odor, turbidity, and oxygen consumed, but these have no very great bearing on the mineral character of the water and with the exception of turbidity are not reported unless quite unusual.

It is the practice in this laboratory to report both ions and hypothetical combinations. The reason for this is that there are several methods of making hypothetical combinations, no one of which is accepted as standard. The values in parts per million for the ions are converted to equivalents, and hypothetical combinations are made beginning at the soluble end of the series.

The method of making calculations will be seen from the accompanying typical data sheet.

Analyst \_\_\_\_\_ Date Started \_\_\_\_\_ Date Finished \_\_\_\_\_ Lab. No. \_\_\_\_\_

Iron—	Sample c.c.	50	Reading	× 2	p.p.m. Fe	× 1.4298	p.p.m. Fe <sub>2</sub> O <sub>3</sub>
Filtered		50	"	× 2	p.p.m. Fe	× 1.4298	p.p.m. Fe <sub>2</sub> O <sub>3</sub>
Unfiltered	"	100	"	× 1	p.p.m. Mn	× 1.29	p.p.m. MnO
Manganese—	"	50	"	× 1	p.p.m. SiO <sub>2</sub>		
Silica—					p.p.m.		
Turbidity							
Alkalinity, Phth.	M. O.				Total Hardness (Ca Eq. + Mg Eq.) × 50		p.p.m.

Positive Ions	Negative Ions	
I. Calcium (200 c.c.)	I. Sulphate (200 c.c.)	
KMnO <sub>4</sub> c.c.		
× _____	Wt.	
	BaSO <sub>4</sub>	
	× 42.8	2057
II. Magnesium (200 c.c.)		
Wt.	II. Nitrate	
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Nitrate N.	
× 89.8	× .0714	4.426
III. Ammonium	III. Chloride	
Ammonia N	P.p.m. ×	0.0282
× 0.0714	to Equivs.	
IV. Sodium (By Diff.)	IV. Carbonate	
Equivs. × 23 to	Alk. ×	.02
p.p.m.	to Equivs.	
	V. Silicate	
	P.p.m. SiO <sub>2</sub>	1.2664
	× .0333	
		Total



## HYPOTHETICAL COMBINATIONS

P.P.M.  $\times$  0.0583 = GRS. PER GAL.

FACTOR

EQUIVALENT

SALT

NaNO <sub>3</sub>	85.01	
NaCl	58.46	
Na <sub>2</sub> SO <sub>4</sub>	71.03	
Na <sub>2</sub> CO <sub>3</sub>	53.00	
NH <sub>4</sub> NO <sub>3</sub>	80.05	
NH <sub>4</sub> Cl	53.50	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	66.07	
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	48.02	
Mg(NO <sub>3</sub> ) <sub>2</sub>	74.17	
MgCl <sub>2</sub>	47.62	
MgSO <sub>4</sub>	60.19	
MgCO <sub>3</sub>	42.16	
CaCl <sub>2</sub>	55.50	
CaSO <sub>4</sub>	68.07	
CaCO <sub>3</sub>	50.04	
CaSiO <sub>3</sub>	58.07	
Fe <sub>2</sub> O <sub>3</sub>		
MnO		
SiO <sub>2</sub>		
Total		
Residue on Evaporation		

Date Commenced _____			Turbidity _____
Dish and Residue _____			Color _____
Dish _____			Odor _____
Sample (100 c.c.) _____ $\times 10,000$			Residue _____ p.p.m.
Sample c.c. _____ 50	Stan. AgNO <sub>3</sub> c.c. _____ $\times 10$	Chlorides _____ p.p.m.	
Sample c.c. _____ 50	N-50 H <sub>2</sub> SO <sub>4</sub> c.c. _____ $\times 20$	Alk. Phth. _____ p.p.m.	
Sample c.c. _____ 50	N-50 H <sub>2</sub> SO <sub>4</sub> c.c. _____ $\times 20$	Alk. M. O. _____ p.p.m.	
Sample c.c. _____ 100	Stan. KMnO <sub>4</sub> c.c. _____ $\times 1$	O. Consumed p.p.m. _____	
Sample c.c. _____ 500	Vol. Dist. _____ 100	Vol. Read. _____ 50	Rdg. _____ $\times .04$
125	100	50	$\times .16$
100	100	50	$\times .20$
Sample c.c. _____ 50	Stan. c.c. _____ 50	$\times .01$	
			Ammonia N. _____ p.p.m.
			Org. N. _____ p.p.m.
			Nitrate N. _____ p.p.m.
			Nitrite N. _____ p.p.m.
Date Completed _____			Chemist _____

**DETERMINATION OF PHOSPHATE IN BOILER WATER<sup>3</sup>**

In boiler-water treatment it is often advisable to use phosphate. In order to control the use of phosphate, it is also advisable to be able to determine rapidly, and with a fair degree of accuracy, the soluble phosphate in the boiler water at frequent intervals. The application of this method is intended for use on boiler-water samples, although, if organic matter is present in sufficient amounts to cause a marked coloration of the water, or if the silicate content is high, the method cannot be used.

The test is dependent upon the fact that molybdenum present as phosphomolybdic acid may be reduced in the presence of an excess of molybdic acid. The reducing agent used is hydroquinone. If hydroquinone is added to an acid solution of molybdic acid, no phosphate being present, the solution will be colorless when treated with alkaline sulphite; but if phosphate is present, phosphomolybdic acid is formed and reduced, giving a blue color. As small an amount as five p.p.m. of phosphate gives a distinct blue color in this test.

**APPARATUS AND SOLUTIONS**

1. Glass funnels and filter paper.
2. Three 250-c.c. volumetric flasks.
3. 10-c.c. and 5-c.c. pipettes.
4. 50-c.c. graduated cylinder.

**Molybdic Acid Solution.**—This solution is made from 125 grams of pure ammonium molybdate dissolved without heat in about two liters of phosphate-free distilled water to which 75 c.c. of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) are slowly added and the volume made up to, roughly,  $2\frac{1}{2}$  liters. A slight blue coloration does not hinder the use of this solution.

<sup>3</sup> Straub, Frederick G., Embrittlement in Boilers: University of Illinois Engineering Experiment Station, Bulletin No. 216, 1930, p. 124.

**Hydroquinone Solution.**—To prepare this solution 50 grams of pure hydroquinone are dissolved in about  $2\frac{1}{2}$  liters of phosphate-free distilled water and 3 c.c. of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) added.

**Carbonate-Sulphite Solution.**—To six liters of distilled water add 1500 grams of commercial soda ash. Dissolve 225 grams of sodium sulphite in 1500 c.c. of water and add to the soda-ash solution.

**Stock Solution of Phosphate.**—Pure monopotassium phosphate is finely ground, dried at  $105^\circ \text{C}$ . for three hours, cooled, and kept in desiccator. Of this salt .1432 gram is dissolved in distilled water, 5 c.c. of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) added, and the volume made up to one liter in a volumetric flask with distilled water. One cubic centimeter of this solution contains one-tenth of a milligram of phosphate ( $\text{PO}_4^{=}$ ).

**Sulphuric Acid Solution.**—Sulphuric acid solution, mentioned later, is made by adding 300 c.c. of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) to about 2200 c.c. of distilled water. This is labeled  $\text{H}_2\text{SO}_4$ .

#### DETERMINATION OF PHOSPHATE

Three 250-c.c. volumetric flasks are required. Into the first measure 50 c.c. of the filtered sample of boiler water. By a pipette 10 c.c. of the standard phosphate solution are delivered into the second flask and 20 c.c. into the third flask. Add to each flask, in succession, 10 c.c. of sulfuric acid, 5 c.c. of molybdic acid and 5 c.c. of hydroquinone solution. Allow the reactions to proceed for five minutes, then add to each flask 15 c.c. of the carbonate sulphite solution, agitate each flask to mix the reagents, and fill each flask to the 250-c.c. mark with distilled water.

Place the flask containing the sample of boiler water between the two flasks containing the standard solutions and compare colors. If the color is lighter than the flask containing the 10 c.c., the  $\text{PO}_4^{=}$  content is less than 20 p.p.m. If the color is between that of the one containing the 10 c.c. and

that of the one containing 20 c.c., the content is between 20 and 40 p.p.m. If the color is darker than that of the one containing 20 c.c., the content is over 40 p.p.m.

Different maximum and minimum values may be established by changing the amount of standard phosphate solution used, and the  $\text{PO}_4^{=}$  content should be within a possible error of about 10 per cent.

#### MINERAL WATER ANALYSIS

Professor Chandler of Columbia University used to say somewhat facetiously that he was the only chemist who had ever made a *complete* water analysis, pointing out that the usual analysis was applied to certain dissolved constituents only. The following system of analysis is referred to colloquially as a "complete mineral," although it would not meet Professor Chandler's requirement that it account for 100 per cent of the original sample.

These methods have been used and modified in the laboratories of the Illinois State Water Survey during a period of more than twenty-five years, and are based on what is believed to be the best current practice.

The object of this method of analysis is to furnish the most complete information possible concerning the composition of mineral solids.

It is applied to medicinal waters most commonly, but should also be made as a final check on any large water supply.

**Complete Minerals.**—The sample is well shaken (except in rare cases of a new well not yet flushed out), and sufficient water taken to yield a residue of .4 to .6 gram as calculated from the predetermined residue (see sanitary analysis, p. 31), thus:

Residue, P.p.m.	C.c. Used
200– 600	1000
600–1200	500
1200–2400	250
2400–6000	100

**Silica.**—Having decided upon the quantity to use, two such portions are measured into volumetric flasks, acidified with HCl (5 c.c. conc. HCl per liter of sample), and evaporated to dryness in platinum dishes. When all the sample has been evaporated, the dry residues are moistened with a few cubic centimeters of concentrated HCl, and again dried on the steam bath. This dehydrates about 90–95 per cent of the silica present. Better dehydration is obtained at 110° C., but care must be taken not to exceed 120° C. or magnesium silicate will form and, on subsequent acidification, pass through the filter.

The residue is then taken up with several portions of hot 1:1 HCl, which are successively poured through a quantitative paper (warming and stirring of each portion aids in extracting the residue, and is essential for waters containing CaSO<sub>4</sub>). Finally, the remaining residue is transferred on to the filter and the dish thoroughly scoured out with a rubber policeman. The paper is washed three times with hot water. The two such papers from each portion are folded together and burned off in the muffle in a weighed platinum or palau crucible. The ignited residue, consisting of silica with traces of heavy metals, barium sulphate, silicates, etc., is weighed, moistened with two or three drops of H<sub>2</sub>SO<sub>4</sub>, about half a cubic centimeter of HF added, and the SiO<sub>2</sub> volatilized on the hot plate under a hood. When dry, the crucibles are again ignited in the muffle, cooled and weighed.

$$\text{crucible} + \text{ignited precipitate} = x$$

$$\text{crucible} + \text{residue after HF} = y$$

$$\text{crucible alone} = z$$

$$x - y = \text{SiO}_2$$

$$y - z = \text{silica bases (non-volatile matter)}.$$

**R<sub>2</sub>O<sub>3</sub>.**—The filtrates from the silica separation are evaporated (if necessary) to about 100 c.c., a few cubic centimeters of bromine water added, and the heating continued until a drop of methyl red added is not decolorized

(i.e., no free Br). The solution is then made just alkaline with  $\text{NH}_4\text{OH}$ . The neutral point of methyl red ( $p\text{H}$  5.8) is just about the point of maximum precipitation of aluminum. After a few minutes' digestion, boiling or nearly boiling, the precipitated  $\text{R}_2\text{O}_3$  is filtered off on quantitative paper and washed with hot water. The two papers from each sample are folded together and ignited in the crucible used above (after  $\text{HF}$  treatment). After cooling and weighing, the residue is treated with  $\text{H}_2\text{SO}_4 + \text{HF}$  as stated to volatilize the  $\text{SiO}_2$  which has escaped the first separation (*Note:* The  $\text{SiO}_2$  is not wholly carried down with the  $\text{R}_2\text{O}_3$ , but a total separation of 98 to 99 per cent can be expected and on a silicate content of only a few parts per million, the remaining 1 to 2 per cent is negligible):

$$\begin{aligned} \text{crucible} + \text{R}_2\text{O}_3 &= m \\ \text{crucible} + \text{R}_2\text{O}_3 \text{ after HF} &= n \\ \text{crucible alone} &= y \text{ (from above).} \\ m-n &= \text{R}_2\text{O}_3 \text{ (Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{phosphates, etc.).} \\ n-y &= \text{silica (to be added to } x-y \text{ above).} \end{aligned}$$

(*Note:* For both  $\text{SiO}_2$  and  $\text{R}_2\text{O}_3$  the ignition of both papers from each separation is advocated rather than saving one for a possible subsequent check; such a check is very rarely needed, and with such small amounts of substance the accuracy of weighing is materially increased by combining the two portions.)

From this point the two filtrates serve different purposes: the one, conveniently marked *A*, is used for the determination of Ca and Mg, and the other, *B*, for  $\text{SO}_4$ , Na and K.

**Calcium.**—Filtrate *A* is acidified with  $\text{HCl}$  and evaporated (if necessary) to about 100 c.c., made alkaline with  $\text{NH}_4\text{OH}$ , and sufficient ammonium oxalate (saturated solution) added to precipitate all the calcium and convert all the magnesium into the oxalate. (*Note:* if no evaporation is necessary prior to this separation, a few cubic centimeters of  $\text{HCl}$  should be added anyway before neutralization with

$\text{NH}_4\text{OH}$  in order to insure a sufficiently high concentration of ammonium salts to hold the magnesium in solution.)

After digesting, preferably half an hour, the calcium oxalate is filtered off on a quantitative paper, and washed with hot 1 per cent ammonium oxalate. The precipitate is then dissolved into a clean beaker with hot 1:1  $\text{HCl}$ , and the  $\text{Ca}^{++}$  again precipitated by making alkaline and adding a cubic centimeter of ammonium oxalate. The precipitate is filtered off and washed as before (the filtrates are combined), ignited in the muffle in a platinum or palau crucible, and weighed *immediately* on cooling as  $\text{CaO}$ .

The amount of  $\text{Ca}^{++}$  is very small, and this double precipitation is absolutely necessary. With this procedure some  $\text{Mg}$  is always occluded, the amount being directly proportional to the concentration of nondissociated magnesium oxalate in solution. Since the amount of  $\text{Mg}$  is unknown, its dissociation cannot be controlled, and an excess of ammonium oxalate is always used to reduce the solubility of the  $\text{CaC}_2\text{O}_4$  (6.8 milligrams per liter at  $25^\circ \text{C}$ .) even though it does depress this dissociation; hence, occlusion is inevitable and double precipitation necessary for accuracy.

**Magnesium.**—The combined filtrates from the  $\text{Ca}^{++}$  separation (cooled if necessary to room temperature) are treated with 20 c.c. saturated microcosmic-salt solution, 8 to 10 drops of thymol-blue indicator are added followed by enough  $\text{NH}_4\text{OH}$  with vigorous stirring, to give a deep blue color. After six hours (preferably overnight) the magnesium ammonium phosphate is filtered off on a paper, washed four times with "magnesia wash" (described under Boiler-Water Analysis, p. 115), and the filtrate discarded. (*Note:* With highly mineralized waters it is advisable to save this filtrate, add a few cubic centimeters more microcosmic-salt, and allow it to stand overnight to insure complete precipitation.)

The precipitate is dissolved from the filter paper back into the same beaker with the least possible hot 1:1  $\text{HCl}$ ;



the paper thoroughly washed and discarded. To the solution add 1 c.c. microcosmic-salt solution, a few drops of thymol-blue indicator, and then make distinctly alkaline by adding ammonia slowly with constant stirring. After standing at least six hours, or preferably overnight, filter off on a weighed Gooch crucible, thoroughly wash with "magnesia wash," ignite to the pyrophosphate in the muffle, and weigh as such.

**Sulphate.**—Filtrate *B* is neutralized with concentrated HCl and then  $\frac{1}{2}$  c.c. added in excess, and the  $\text{SO}_4^{=}$  precipitated in the boiling solution with a slight excess of 10 per cent  $\text{BaCl}_2$  added drop by drop with constant stirring. After digesting until the  $\text{BaSO}_4$  has settled, another drop of  $\text{BaCl}_2$  is added to make sure the precipitation is complete, and the  $\text{BaSO}_4$  filtered off on a weighed Gooch crucible, washed with hot water, ignited in the muffle, and weighed.

This method gives strictly accurate results only in the absence of alkali salts, and then only by compensation of errors: the undissociated  $\text{HSO}_4$  gives compounds of the type  $\text{Ba}(\text{HSO}_4)_2$  and  $(\text{BaCl})_2\text{SO}_4$  which decompose on ignition with the loss of HCl and  $\text{H}_2\text{SO}_4$ ; sufficient  $\text{BaCl}_2$  is usually occluded, however, to offset this. The presence of excess HCl is detrimental, not because of its solvent effect on the  $\text{BaSO}_4$ , but because it seriously influences the composition of the precipitate. In the presence of alkali salts (especially KCl), the results are always low unless the proportion of Na:K is at least 4:1. A solution containing not over 10 per cent  $\text{BaCl}_2$  must be used for precipitation, otherwise the composition of the precipitate is indefinite and not reproducible.

**Sodium and Potassium.**—The whole filtrate from the  $\text{SO}_4^{=}$  separation (or an aliquot portion representing .2 to .3 gram of alkali chlorides) is used for the determination of  $\text{Na}^+$  and  $\text{K}^+$ .

The solution is evaporated to dryness in a platinum dish and further dried at  $110^\circ\text{C}$ . to  $120^\circ\text{C}$ . in the oven (to

prevent decrepitation on ignition). It is then ignited at not over *dull* red to expel the  $\text{NH}_4$  salts, the residue taken up with 10 to 15 c.c. hot water, and sufficient saturated  $\text{Ba}(\text{OH})_2$  solution added to form a thin film or pellicle on the surface of the liquid. The resulting precipitate is filtered off, well washed with hot water, and discarded. The filtrate is evaporated to 15 to 20 c.c. and ammonium carbonate added to the warm solution as long as a precipitate forms. This is filtered off, washed, and discarded. The filtrate is evaporated to dryness in a palau dish, ignited to expel the  $\text{NH}_4$  salts, and again treated with  $\text{Ba}(\text{OH})_2$ , followed by  $(\text{NH}_4)_2\text{CO}_3$  as stated.

After again evaporating (in a palau dish) and igniting off the  $\text{NH}_4$  salts, the residue is taken up in hot water, filtered (to remove carbon resulting from decomposition of carbonate in the  $(\text{NH}_4)_2\text{CO}_3$ ) into a weighed palau dish, a drop of  $\text{HCl}$  added, evaporated to dryness, dried in the oven or gently ignited, and the combined chlorides ( $\text{Na} + \text{K}$ ) weighed.

Before proceeding to separate  $\text{K}$ , the analysis should be partially figured up assuming zero potassium to see (a) if the sums of the positive and negative equivalents nearly check, and (b) if the positives and negatives combined in the order of hypothetical combinations leave an amount of  $\text{Ca}$  (or  $\text{Ca} + \text{Mg}$ ;  $\text{MgCO}_3 \times 1.19 = \text{CaCO}_3$ ) as carbonate which checks the alkalinity reasonably well. If not, the alkalis are either further purified or redetermined.

If a suitable balance is obtained (remembering that the positive equivalents decrease when  $\text{K}$  is separated), the combined chlorides are taken up in a little water, a drop of  $\text{HCl}$  added, and sufficient chloroplatinic acid to convert all the alkalis into chloroplatinates (1 c.c. of a solution containing 10 grams  $\text{PtCl}_4$  in 100 c.c. for each 30 mg. of combined chlorides). The mixture is evaporated to complete dryness on the steam bath. The dry residue is taken up with 95 per cent alcohol, each extraction being poured through a paper, and finally the remaining potassium

chloroplatinate is transferred to the paper and washed with 95 per cent alcohol until the filtrate comes through colorless. Allow the alcohol to evaporate from the paper (subsequent evaporation if alcohol were present would reduce the K salt in part to metallic platinum), and then the K salt is dissolved into a weighed palau dish with hot water. The solution is evaporated to complete dryness, dried an hour in the oven at  $110^{\circ}\text{C}.$ , and weighed. (*Note:* platinum residues and alcohol washes are saved in the Pt residue bottle.)

$$\text{K}_2\text{PtCl}_6 \times 0.3068 = \text{KCl}$$

$$\text{Combined chlorides} - \text{KCl} = \text{NaCl}$$

The factor .3068 is the theoretical relation and never attained in practice; a more accurate figure for the procedure probably would be .3060, but, strictly speaking, each analyst should determine his own factor by a blank run on C. P. salts, since it depends upon the technique used.

Portions of the original sample are used for the determination of iron, manganese, and (when necessary) residue, chloride, and alkalinity.

**Iron.**—If the sample contains iron in suspension, a portion containing not over .4 mg. Fe is boiled with HCl to effect solution of the iron, filtered if necessary, and diluted to 50 c.c. in a Nessler tube. If low in iron, 50 c.c. are measured directly into a Nessler tube. One cubic centimeter of concentrated HCl is added, followed by three drops of  $\text{KMnO}_4$  solution (6.32 grams per liter), the tube mixed by inverting and allowing to stand ten minutes. If decolorization ensues, a drop or two more  $\text{KMnO}_4$  is necessary. Five cubic centimeters of KSCN solution (20 grams per liter) are then added, the contents mixed, and compared at once with standards made simultaneously by measuring out .1, .3, .5, .7, .9, 1.1, etc., c.c. portions of standard iron solution (diluting to 50 c.c.) and treating exactly as stated.

The cubic centimeters of standard iron solution in the

tube, which matches the sample, multiplied by 2 gives parts per million of Fe, if 50 c.c. of sample are used.

**Manganese.**—Fifty or 100 c.c. of sample are measured into a beaker,  $\frac{1}{2}$  to 1 c.c. of concentrated  $\text{HNO}_3$  added, and the solution heated nearly to boiling. Sufficient  $\text{AgNO}_3$  solution (20 grams per liter) is now added to precipitate all the chloride and leave 1 c.c. of  $\text{AgNO}_3$  in excess. If the chloride precipitate is heavy, it is filtered off, washed and discarded. If only slight, it may be neglected because the ammonium persulphate added will dissolve it. (For waters very high in chlorides, see procedure given for salt brines, p. 133.) Then .5 gram ammonium persulphate crystals is added to each and the solutions kept warm for ten minutes. If any pink color develops, the solution is transferred to a Nessler tube and compared with standards made up simultaneously by measuring out .2, .4, .6, .8, 1.0-c.c. portions of standard manganese solution and treating as stated (including the addition of 1 c.c. of  $\text{AgNO}_3$ , since this is necessary to catalyze the oxidation).

For a 100-c.c. sample, the cubic centimeters of standard manganese solution in the comparison tube are equal to parts per million Mn in the sample.

**Residue.**—Sufficient sample to give about 50 mg. residue is evaporated to dryness in a weighed glass or platinum dish, dried at  $180^\circ \text{C}$ . for one hour, and weighed.

**Chlorides.**—For chlorides not exceeding 100 p.p.m., 50 c.c. of the sample is measured out, 1 c.c.  $\text{K}_2\text{CrO}_4$  solution (50 grams per liter) added, and the chloride titrated with  $\text{AgNO}_3$  solution (1 c.c. = .5 mg. Cl) to a distinct reddish-brown end point.

$$\text{c.c. AgNO}_3 \times 10 = \text{p.p.m. Cl.}$$

If the chlorides are higher than 100 p.p.m., a portion of the sample may be diluted up to a definite volume and an aliquot part titrated. If very high, the Volhard method described for salt brines (p. 133), is recommended.

**Alkalinity.**—To 50 c.c. of the sample add 3 drops of

methyl orange indicator and titrate with N/50  $\text{H}_2\text{SO}_4$  solution. Cubic centimeters N/50  $\text{H}_2\text{SO}_4 \times 20 =$  p.p.m. alkalinity as  $\text{CaCO}_3$ .

Phenolphthalein alkalinity, if present, is reported on the mineral sheet separately, but, of course, the methyl orange alkalinity includes this also.

**Calculation.**—The mineral sheet is the only original and permanent record of the analysis, all entries on it are therefore in ink.

The parts per million of the ions are reported to the nearest tenth, and the equivalents to three decimal places.

The hypothetical combinations are formed by adding or subtracting the equivalents in the following order, the resulting equivalents of each salt are then multiplied by

Salt	Equivalent Weight	Log
$\text{KNO}_3$ .....	85.11	.9300 (only included if over .1 p.p.m.)
$\text{KNO}_2$ .....	101.11	.0048
$\text{KCl}$ .....	74.56	.8725
$\text{K}_2\text{SO}_4$ .....	87.13	.9402
$\text{K}_2\text{CO}_3$ .....	69.14	.8397
$\text{NaNO}_3$ .....	85.01	.9295
$\text{NaCl}$ .....	58.46	.7668
$\text{Na}_2\text{SO}_4$ .....	71.03	.8514
$\text{Na}_2\text{CO}_3$ .....	53.00	.7243
$\text{NH}_4\text{NO}_3$ .....	80.13	.9038
$\text{NH}_4\text{Cl}$ .....	53.47	.7281
$(\text{NH}_4)_2\text{SO}_4$ .....	66.04	.8198
$(\text{NH}_4)_2\text{CO}_3$ .....	48.01	.6813
$\text{Mg}(\text{NO}_3)_2$ .....	74.13	.8702
$\text{MgCl}_2$ .....	47.62	.6778
$\text{MgSO}_4$ .....	60.18	.7795
$\text{MgCO}_3$ .....	42.16	.6249
$\text{CaCl}_2$ .....	55.49	.7742
$\text{CaSO}_4$ .....	68.06	.8329
$\text{CaCO}_3$ .....	50.00	.6990

the equivalent weight of that salt to give parts per million (reported to the nearest tenth). The parts per million by multiplying by .0583 are converted into grains per gallon.

The total parts per million of the hypothetical combinations should check the determined residue within the following limits: *C* represents the calculated residue (sum of hypotheticals) and *D* the determined residue; the column headed per cent gives the allowable error between the positive and negative ions:

Residue	<i>C</i> - <i>D</i> , p.p.m.	<i>D</i> - <i>C</i> , p.p.m.	Per Cent
0 to 50	5	15	15
50 to 100	6	20	7
100 to 200	8	30	5
200 to 500	12	40	4
500 to 1000	15	50	3
1000 to 2000	22	64	2

#### CHLORIDE DETERMINATION ON SALT BRINE

**Approximate Determination.**—A rough determination of chloride is conducted as follows, preferably before the mineral analysis is started:

Ten cubic centimeters of the sample are diluted to 100 c.c. in a volumetric flask; after mixing, 5 c.c. are withdrawn into a clean beaker containing about 75 c.c. of distilled water; 1 c.c. of concentrated  $\text{HNO}_3$  added, then 10 c.c. of (approx.)  $\text{N}/10 \text{ AgNO}_3$  introduced from a pipette. After gently warming and vigorously stirring to coagulate the precipitate, 1 c.c. of ferric alum is added, and the solution titrated with (approx.)  $\text{N}/10 \text{ KSCN}$  to the first permanent reddish brown tinge.

c.c.  $\text{KSCN} \times \text{factor} = \text{c.c. AgNO}_3 \text{ excess};$

10-c.c. excess = c.c.  $\text{AgNO}_3$  used by chloride;

c.c. used  $\times \text{factor} \times 2000 = \text{p.p.m. Cl}^- \text{ in sample (approximately).}$

**Final Determination.**—The sample is sufficiently diluted so that the portion taken for analysis gives about .3 gram

of  $\text{AgCl}$  or uses up a little less than 25 c.c. of  $\text{AgNO}_3$ . For dilutions see table on p. 118.

The dilutions are made one at a time using flasks and pipettes reserved for this purpose, keeping as nearly as possible to a uniform temperature of  $23^\circ \text{C}$ . The portion taken for analysis is measured into a 250-c.c. pyrex beaker, distilled water added to make approximately 50 c.c. (where necessary), 1 c.c. of conc.  $\text{HNO}_3$  added, followed by 25 c.c. (or 50 c.c. if chloride is over 64,000) of  $\text{AgNO}_3$ , measured from a pipette reserved for this purpose.

The beakers are warmed on the hot plate and vigorously stirred to coagulate the  $\text{AgCl}$ . The supernatant liquor is poured off through a weighed Gooch crucible, the precipitate washed twice by decantation with hot dilute  $\text{HNO}_3$  (2 c.c. conc.  $\text{HNO}_3$  in 100 c.c. water), and then transferred to the Gooch crucible with the aid of a policeman. After two more washings, the crucible is dried at  $115$  to  $125^\circ \text{C}$ . for at least twenty-four hours, cooled and weighed.

$$\begin{aligned}\text{Weight of AgCl} \times 247.38 (\log 2.39337) &= \text{mg. Cl}^-; \\ \text{mg. Cl} \times \text{multiplier (from table)} &= \text{p.p.m. Cl}^-.\end{aligned}$$

The filtrate and washings are caught in a 300-c.c. Erlenmeyer flask, 1 c.c. ferric alum added, and the excess of  $\text{AgNO}_3$  titrated with  $\text{KSCN}$  to the first permanent reddish brown color.

$$\begin{aligned}\text{c.c. KSCN} \times \text{factor} &= \text{c.c. AgNO}_3 \text{ in excess;} \\ 25 \text{ (or 50)} - \text{c. c. excess} &= \text{AgNO}_3 \text{ used;} \\ \text{c.c. AgNO}_3 \text{ used} \times \text{factor} \times \text{multiplier} &= \text{p.p.m. Cl}.\end{aligned}$$

The results obtained by the gravimetric and by the volumetric method should not differ by more than .4 per cent (when the difference between them times 100 is divided by their average), and is usually about .1 per cent. The two results, if satisfactory, are averaged and this average accepted as the chloride content of the sample.

Gravimetric.....	67,190 p.p.m.	Gravimetric.....	25,362 p.p.m.
Volumetric.....	67,372	Volumetric.....	25,315
<hr/>		<hr/>	
Average.....	67,281 p.p.m.	Average.....	25,338 p.p.m.
Error $182 \times 100 / 67,281$		Error $47 \times 100 / 25,338$	
= 0.21 per cent		= 0.14 per cent	

Silver chloride precipitates and residues from the Gooch crucibles are put in the silver residue bottle.



## CHAPTER IV

### LABORATORY EXERCISES IN WATER TREATMENT

#### Experiment I

##### WATER-SOFTENING REQUIREMENTS

- A. The experiment as outlined is designed to illustrate the lime and soda softening process and various modifications of this process.
1. Unmodified lime-soda treatment.
  2. Partial softening (removal of  $\text{Ca}(\text{HCO}_3)_2$  only).
  3. Excess treatment with soda.
  4. Split treatment.
  5. Use of alum.
  6. Use of sodium aluminate.
  7. Hot process.
  8. Recarbonation after softening.
- B. Two samples of water are used in the experiment: (a) with no noncarbonate hardness; and (b) with noncarbonate hardness. These two waters are easily obtainable and serve to demonstrate the points.
- C. Class is to calculate cubic centimeters of reagents required to soften 200 c.c. of each water. Use lime water such that 1 c.c.  $\equiv$  5.6 mg. of 100 per cent  $\text{CaO} \equiv .2$  milliequiv. and soda ash such that 1 c.c.  $\equiv$  10.6 mg. of 100 per cent  $\text{Na}_2\text{CO}_3 \equiv .2$  milliequiv. then number of equivalents required = number of cubic centimeters of reagent required per 200 c.c.

D. The following analyses may be used to illustrate the calculation of softening requirements:

University Tap Water		University Tap Water + 246 p.p.m. MgSO <sub>4</sub> ·7 H <sub>2</sub> O
	P.p.m.    Milli- equiv.	P.p.m.    Milli- equiv.
Na.....	30.2 = 1.3	30.2 = 1.3
Ca.....	64. = 3.2	64. = 3.23
Mg.....	30. = 2.47	55. = 4.53
Alk.....	338. = 6.76	338. = 6.76
CO <sub>2</sub> .....	11. = .5	11. = .5
SO <sub>4</sub> .....	.7 = .014	96.7 = 2.01
Cl.....	8.0 = .23	8.0 = .23
Total hardness.....	283.0	386

Calculation of water-softening requirements (analysis reported in milliequivalents).

Lime requirement, (CaO) (90 per cent pure) lb. per thousand gallons.

$$(\text{CO}_2 + \text{Mg}^{++} + \text{Alk.}) \times 28 \times .0083 \times 1.11 = \text{lb. CaO/M gal.}$$

or

$$[\text{Na}^+ + (\text{Ca}^{++} + 2 \text{Mg}^{++} + \text{CO}_2 - (\text{SO}_4^{--} + \text{Cl}^-))] \times 28 \times .0083 \times 1.11 = \text{lb. CaO/M gal.}$$

Soda-ash requirements, Na<sub>2</sub>CO<sub>3</sub> (58 test soda-ash approx. 100 per cent pure).

$$(\text{Ca}^{++} + \text{Mg}^{++} - \text{Alk.}) \times 53 \times .0083 = \text{lb. of Na}_2\text{CO}_3 \text{ needed per thousand gallons.}$$

or

$$[(\text{Ca}^{++} + \text{Mg}^{++}) - (\text{CO}_3^{=})] \times 53 \times .0083 = \text{lb. of Na}_2\text{CO}_3 \text{ needed per thousand gallons.}$$

## E. Calculation.

## 1. Unmodified process.

## (a) University tap water.

*Lime required*

$$(.5 + 2.47 + 6.76) = 9.73 \text{ milliequiv. per liter}$$

$$\frac{9.73}{5 \times .2} = 9.73 \text{ c.c. of lime water per 200 c.c.}$$

$$1 \text{ c.c.} = .2 \text{ milliequiv.}$$

No soda ash required.

(b) University tap water +  $\text{MgSO}_4$ .*Lime required*

$$(.5 + 4.53 + 6.76) = 11.79 \text{ milliequiv. per liter}$$

$$\frac{11.79}{5 \times .2} = 11.79 \text{ c.c. lime water per 200 c.c.}$$

*Soda ash required*

$$(3.23 + 4.53 - 6.76) = 1.0 \text{ milliequiv. per liter}$$

$$\frac{1.0}{5 \times .2} = 1.0 \text{ c.c. soda ash per 200 c.c.}$$

2. Partial softening (removal of  $\text{Ca}(\text{HCO}_3)_2$  only)

## (a) University tap water.

*Lime required*

$$\text{Ca}^{++} + \text{CO}_2 = 3.7 \text{ milliequiv. } \therefore \text{ need } 3.7 \text{ milliequiv. per liter}$$

$$\frac{3.7}{5 \times .2} = 3.7 \text{ c.c. of lime water per 200 c.c.}$$

No soda ash

(b) University tap water +  $\text{MgSO}_4$ .

Same as 2(a).

## 3. Excess treatment.

## (a) Use theoretical lime water + 1 c.c. excess

## (b) Use theoretical lime water + 2 c.c. excess

Use theoretical soda ash + 1 c.c. excess

## 4. Split treatment (calculate as in 1(a) and 1(b)).

## 5. Use of alum. Lime and soda calculated as in 1(a) and 1(b). Use theoretical amounts of reagents plus 1 grain

- per gallon of alum (1 c.c. alum solution per 100 c.c. = 1 grain per gallon).
6. Use of sodium aluminate. Lime and soda calculated as in 1(a) and 1(b). Use theoretical amounts of reagents plus 1 grain per gallon of  $\text{Na}_2\text{Al}_2\text{O}_4$ . (1 c.c.  $\text{Na}_2\text{Al}_2\text{O}_4$  sol. per 100 c.c. = 1 grain per gal.)
  7. Hot process (calculate as in 1(a) and 1(b)).
  8. Recarbonation (calculate as in 1(a) and 1(b)).

#### F. Laboratory Directions.

1. (a) Add 200-c.c. sample to a 400-c.c. beaker.  
 (b) Add required amounts of reagents—mix well—note floc.  
 (c) Allow to settle two hours.  
 (d) Decant through a fluted filter.
2. Same as 1. Note less reagent.
3. Same as 1. Note excess reagent.
4. (a) Add total amount of reagent to 150 c.c. of sample.  
 (b) Allow to stand half an hour.  
 (c) Add 50 c.c. more of the sample—mix well.  
 (d) Allow to settle an hour and a half.  
 (e) Decant through filter, etc.
5. Same as 1—Adding 1 grain per gallon of alum (1 c.c. alum solution per 100-c.c. sample).
6. Same as 1—Ditto sodium aluminate.
7. Same as 1—Heat to 60° C.—Then add reagents (allow to stand half an hour).
8. (a) Treat as in 1.  
 (b) Split the filtrates into two portions.  
 (c) Pass  $\text{CO}_2$  into one portion of each sample till phenolphthalein alkalinity has disappeared.  
 (d) Set both portions of each sample away till next day.  
 (e) Note any after precipitation on the following day.

- #### G. 1. Decant sample through filter (recarbonation samples stand over till next day).
2. Run total hardness and alkalinity.
  3. List results as follows:

	Total Hardness		Alkalinity			
			<i>a</i>		<i>b</i>	
	<i>a</i>	<i>b</i>	Phenol-phthalein	M.O.	Phenol-phthalein	M.O.
1. Theoretical softening.	....	....	.....	....	.....	....
2. Partial softening....	....	....	.....	....	.....	....
3. Excess treatment....	....	....	.....	....	.....	....
4. Split treatment.....	....	....	.....	....	.....	....
5. Theory + alum.....	....	....	.....	....	.....	....
6. Theory + sodium aluminate.....	....	....	.....	....	.....	....
7. Hot process.....	....	....	.....	....	.....	....
8. Recarbonation {	1....	....	.....	....	.....	....
	2....	....	.....	....	.....	....

NOTE.—The students must spend one hour overtime this period.

For next laboratory period they need only come for one hour.

(Student doing No. 8 has to return the following day for his extra hour.)

## Experiment II

### COAGULATION AND FILTRATION

(Two two-hour laboratory periods)

#### A. Materials.

1. Students will each be given a sample of water, preferably a surface water.
2. Each student is given a sample of one of the following clays: Cayuga shale, China clay, No. 10 ball clay, kaolin, No. 3 ball clay. (This series is chosen because it furnishes a good variety of "fat" and "lean" clays which coagulate with varying degrees of ease when their suspensions are treated with alum.)
3. A bottle of coloring matter (tea or other vegetable extract) is provided.

4. Turbidity and color standards are set out by color camera, indicators and standard acid are on the shelf. Jackson turbidimeter for high turbidity.
5. Solutions of alum (1 c.c. in 100 = 1 grain per gallon) and  $\text{Na}_2\text{Al}_2\text{O}_4$  (1 c.c. in 100 = 1 grain per gallon).

B. Procedure for first period.

1. Each student is to add some clay (a pinch or two) and coloring matter to his sample to produce turbidity and color. Shake vigorously.
2. Allow to stand fifteen minutes. Decant into another bottle.
3. Determine turbidity,  $p\text{H}$ , color and alkalinity. The last two on filtered samples.
4. Set up two samples (shake bottle well before using) of 200 c.c. each in 400-c.c. beakers.
5. Add alum to one sample and sodium aluminate to the other.
  - (a) Half grain per gallon, i.e., 1 c.c.
  - (b) Stir vigorously.
  - (c) Allow to stand from five to ten minutes.
  - (d) Note presence of distinct floc at end of (c), if none is noted, repeat (a), (b), and (c).
  - (e) When a good floc is produced, make a note of the amount of reagents used.
6. Cover the beaker with filter paper and allow to stand till next period.

NOTE.—Theoretically, alum reduces alkalinity 8 p.p.m. for each grain per gallon used. Estimate the effect of the alum dose and, if alkalinity is low, then add 1 grain per gallon of lime (1 c.c. of lime solution = 7.6 mg.  $\text{Ca}(\text{OH})_2$  for each 8 p.p.m. that alkalinity will be reduced below 80 p.p.m.

C. Procedure for second period.

1. Shake sample well and set up two samples as before.

2. Add directly the amounts of alum and aluminate respectively that were found best at previous meeting.
3. Stir well and allow to stand an hour and a half.
4. Meanwhile determine the turbidity and  $pH$  of the supernatant liquor in the samples from the previous time (do not filter but *decant carefully*), also filter the remainder and determine alkalinity and color.
5. At the end of an hour and a half determine turbidity and  $pH$  (supernatant liquor decanted), color and alkalinity (filtered) on the sample set up that day.
6. List the results in the following tabular form.

Sample No.	Turbidity	Color	Alkalinity	$pH$	Treatment		
					Lime	Alum	Aluminate
.....	.....	.....	.....	....	....	....	.....

## ALUMINATE COAGULATION

Sample No.	One and One-half Hours				Two Days			
	Turbidity	$pH$	Color	Alkalinity	Turbidity	$pH$	Color	Alkalinity
.....	.....	...	.....	.....	.....	...	.....	.....

## ALUM COAGULATION

Sample No.	One and One-half Hours				Two Days			
	Turbidity	$pH$	Color	Alkalinity	Turbidity	$pH$	Color	Alkalinity
	.....	...	.....	.....	.....	...	.....	.....

It would be advantageous, if this experiment could be carried out in a single period. The samples undergo a change on standing which cannot be completely reversed by vigorous shaking. It would also be advisable to have some members of the class carry out the exercise on samples containing turbidity only and color only.

A. Discuss the tabulated results with reference to these particular points.

1. Relative amounts of alum and aluminate needed.
2. Relative amounts of alumina per lb. of each coagulant.

$$(a) \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} - \frac{101.94}{666.42} = 15.28 \text{ per cent } \text{Al}_2\text{O}_3$$

$$(b) \text{Na}_2\text{Al}_2\text{O}_4 \frac{101.94}{163.93} = 62.2 \text{ per cent } \text{Al}_2\text{O}_3$$

(c) i.e.,  $4.07 \times$  as much  $\text{Al}_2\text{O}_3$  in aluminate as in  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

(d) Aluminate only about 85 per cent, rest is NaOH. Therefore, commercial aluminate contains only about 3.46 times as much  $\text{Al}_2\text{O}_3$  in aluminate as in alum.

3. Relative costs of coagulants.

(a) Alum about \$28 per ton.

(b) Aluminate about \$100 per ton.

4. Difficulties with aluminate in soft waters.

5. Reactions briefly.

(a) Alum ionizes to give  $\text{Al}^{+++}$  which reacts with the  $\text{OH}^-$  to give an insoluble precipitate  $\text{Al}(\text{OH})_3$ .

(b) Aluminate probably forms basic magnesium aluminates and complex calcium alumina silicates.

6. Use of lime in soft and colored waters.

7. Other coagulants.

(a) Lime and iron.

(1) Incrustation.

(b) Chlorinated copperas.



8. Any other points brought by the data.
9. Definition of clays: ball clay, a fat clay, sticky when moist, strong in dry state, stays in suspension well, pH 4.0. China clay, clean clay, not sticky, weak in dry state, pH about 6.0, precipitates easily.

### Experiment III

#### CHLORINATION

##### A. Materials.

1. Two liters of tap water polluted by adding 50 c.c. of sewage or 50 c.c. of fresh lactose broth culture of *B. coli* shortly before class convenes will serve as the water to be treated.
2. Sterile 1-c.c. pipettes, dilution water, melted agar, sterile petri dishes.
3. Orthotolidine solution and chlorine standards.

A fresh solution of chlorine containing as nearly as possible .1 gram per hundred c.c. One c.c. of this solution added to 100 c.c. of water to be disinfected corresponds to a treatment of 1 p.p.m. A burette or pipette graduated in tenths of a cubic centimeter should be available for measuring the chlorine solution used in the treatment. It has been found convenient to prepare first a strong solution of chlorine (about .5 per cent) by bubbling the gas into good distilled water. The strength of this solution is determined by titration against standard thiosulphate in the usual manner. A portion is then diluted for use with the calculated amount of distilled water. One c.c. of the dilute solution may be added to 100 c.c. of distilled water and the free chlorine determined colorimetrically as a final check on the standardization.

##### B. Procedure.

1. Each student is to run 3 plates, a 1 c.c. plate, a 1:10 dilution and a 1:100 dilution.

2. The students will be divided up and run their counts at intervals of one, three, five, ten, fifteen, twenty, and twenty-five minutes after chlorination. One student will run a control, or a count before chlorination, then the next student will plate out one minute after sterilization, etc. (For bacteriological technique, see Chapter V.) A test for *B. coli* should be run fifteen minutes after treatment.
3. Measure out three 100-c.c. portions of the water to be treated and add .5, 1.0 and 1.5 c.c. of chlorine to each, respectively. Determine the residual chlorine (p. 100) after fifteen minutes.
4. Calculate the "chlorine demand" of the water from the data obtained in 3. Treat one liter of the polluted water with sufficient chlorine to correspond to the "demand" plus .2 p.p.m.
5. Samples are taken for bacterial examination as directed in 2. At the end of fifteen minutes after treatment, a residual chlorine test should be run as a check on the treatment.
6. List the results as follows:

Time	Residual $\text{Cl}_2$	Count			<i>B. Coli</i>
		1 c.c.	1:10	1:100	
0					
1					
3					
5					
10					
15					
20					
25					
30					

## CHAPTER V

### BACTERIOLOGICAL EXAMINATION OF WATER

THE water expert of to-day cannot afford to take the risk of basing his opinion upon any one form of inquiry alone, and it behooves him to make himself familiar with all the means of throwing light upon the question at issue.

In consideration of the magnitude of the bacteriological field, it is manifestly out of the question, in a book of this scope, to go very far beyond a simple enumeration of the bacteria present in a cubic centimeter of the water under examination, supplemented by a determination of the probable presence or absence of germs derived from an intestinal source, thus leaving the problem of exhaustive differentiation to be discussed by writers upon bacteriology.<sup>1</sup>

These elementary applications of the science are of especial value for the testing of filters and watching any variation in their efficiency.

For such a purpose the simple count of bacteria per cubic centimeter is most valuable, and differentiation is a secondary matter; the assumption being a just one that a filter which will remove the harmless bacteria may be trusted to take out the objectionable ones as well.

As to the value of the "count of bacteria per cubic centimeter" in the general cases outside of filter examination, much has been asserted to show its uselessness; and for "single-sample" examinations the objections are doubtless well taken, but for "comparative tests," such as watching the distance to which a stream of sewage is felt in a lake, or observing the relation between sedimentation and

<sup>1</sup> The technique of such processes as "staining," "hanging drop," etc., will be found in any good textbook of bacteriology.

river flow, there is no question as to its being of great value.

For the accomplishing of the determinations that are here proposed the following culture media should be carefully prepared and kept ready at hand.<sup>2</sup>

**Nutrient Broth.**—Add 3 grams of Liebig's beef extract and 5 grams of peptone (Digestive Ferments) to one liter of distilled water. Heat on a steam bath until the peptone is dissolved. Restore water lost by evaporation.

All culture media used in water analysis should have a pH between 6.2 and 8.4. This may be checked by adding five drops of phenol sulphon phthalein (phenol red) to 5 c.c. of the media diluted with 5 c.c. of distilled water. A faint pink color indicates the proper reaction. The reaction, if not correct, will in all probability be too acid. In this case add standard NaOH (approximately N/10) to the diluted media until the proper reaction is obtained. Calculate the amount of N/1 NaOH which will produce the same reaction in the known volume of media being tested. Add to the media and recheck reaction. The indicator is prepared by dissolving .04 gram of the dye in 30 c.c. of alcohol and making up to 100 c.c. with distilled water.

Sterilization is then accomplished by heating in an autoclave to fifteen pounds pressure (120° C.) for fifteen minutes.

Keep the broth and all other stock media in a cool, dark, moist place, e.g., an ice box.

---

**Nutrient Gelatin.**—Dissolve 3 grams of Liebig's extract in one liter distilled water. Add

Gelatin . . . . .	100 grams <sup>3</sup>
Peptone . . . . .	5 grams

<sup>2</sup> The formulæ for culture media are largely based upon the recommendations of the special committee of the American Public Health Association.

<sup>3</sup> The gelatin should be dried for half an hour at 105° C. before weighing.

Heat slowly on a water bath at a temperature of 65° C. until all is dissolved. Restore water lost by evaporation. Adjust reaction as described.

Place the finished medium in test-tubes, 10 c.c. in each. Plug the tubes with cotton and sterilize in autoclave and store as described under nutrient broth.

It is best to make but a small quantity of any of the culture media at a time, as they do not keep well in stock.

**Lactose Broth.**—Prepared the same as the ordinary broth except that 5 grams of pure lactose are added with the peptone and beef extract. Its reaction should be adjusted. Sterilize in autoclave as usual.

The best vessels in which to store the medium are the fermentation tubes, in which it is to be used (see p. 158).

**Nutrient Agar.**—When making plate cultures for organisms that develop at blood temperature it becomes necessary to employ a medium with a higher melting point than gelatin possesses.

To make one liter of nutrient agar add 3 grams of Liebig's beef extract, 5 grams of peptone (Difco) and 12 grams of agar (dried at 105° C.) to one liter of distilled water. Heat on water bath until solution is complete. Replace water lost by evaporation. Cool to 45° C. and then reheat to 65° C. and again replace any water loss due to evaporation. Adjust reaction as under nutrient broth. Filter through cotton, using hot-water funnel and place in cotton-plugged test-tubes, 10 c.c. in each tube. Sterilize in autoclave as usual.

**Litmus Solution.**—Prepare a 2 per cent water solution of reagent litmus by adding the powdered litmus to the water, boiling five minutes, replacing loss due to evaporation, filtering and sterilizing in autoclave as usual.

ENDO MEDIUM<sup>4</sup>

**Preparation of Stock Agar.**—Add 5 grams of beef extract, 10 grams of peptone and 30 grams of agar (undried market product as stored in the ordinary laboratory cupboard), to 1000 c.c. of distilled water.

Boil until all the agar is dissolved and then make up the lost weight due to evaporation with distilled water. Titrate and adjust the reaction so that the final pH value will be between 7.8 and 8.2. This agar may then be clarified sufficiently by either one of the following procedures (inasmuch as a 3 per cent agar is rather difficult to filter, and as this particular medium does not have to be entirely free of precipitate, procedure (2) is probably the better one to employ):

**Procedure (1).**—Bring to boil over a free flame, stirring constantly, and filter through cotton or cloth.

**Procedure (2).**—Place a straight-walled container holding the agar in the autoclave and hold at fifteen pounds pressure for fifteen minutes. Shut off the steam and let the agar stand in the autoclave until solidification is complete (overnight if possible). Remove the container from the autoclave, dump the solidified agar on clean paper and cut off the detritus from the bottom and discard. Cut and melt the clear supernatant agar and distribute in 100 c.c. or larger known quantities in flasks large enough to hold the other ingredients which are to be added later. Sterilize in the autoclave at fifteen pounds for fifteen minutes after the pressure reaches fifteen pounds as directed.

**Preparation of Endo Medium Plates.**—Prepare a 10 per cent solution of basic fuchsin in 95 per cent alcohol, allow to stand twenty-four hours, decant and filter the supernatant fluid. This is a stock solution.

When ready to make plates, melt a known portion of the stock agar and to each 100 c.c. of agar add the following ingredients in the order given, mixing thoroughly after the addition of the final reagent:

One per cent of chemically pure lactose in sterile solution, .5 c.c. of the stock basic fuchsin solution (10 per cent alcoholic solution) and .125 gram anhydrous sodium sulphite dissolved in a small amount of hot distilled water. The sulphite solution must be made up fresh each time. Mix thoroughly.

<sup>4</sup>Standard Methods, op. cit.

Pour plates and allow to harden in the incubator before use. Inoculate by streaking on the surface.

#### EOSIN METHYLENE BLUE AGAR

Add 10 grams of Difco peptone, 2 grams of dipotassium phosphate ( $K_2HPO_4$ ) and 15 grams of undried agar to 1000 c.c. of distilled water. Boil until all ingredients are dissolved and make up any loss due to evaporation with distilled water. Adjustment of reaction is not necessary.

Place measured quantities (100 or 200 c.c.) in flasks or bottles and sterilize in the autoclave as directed at fifteen pounds for fifteen minutes.

Just prior to using, melt stock agar and add the following ingredients to each 100 c.c.:

Lactose, sterile 20 per cent solution, 5 c.c.

Eosin, yellowish, 2 per cent aqueous solution, 2 c.c.

Methylene blue, .5 per cent aqueous solution, 2 c.c.

Mix thoroughly, pour into Petri dishes, allow to harden and inoculate by streaking on the surface.

It is allowable to add all the ingredients to the stock agar at the time of preparation, place in tubes or flasks and sterilize. Decolorization of the medium occurs during sterilization. The color returns after cooling.

**Sterilization of empty glassware** is secured by heating for an hour at  $170^{\circ} C$ .

The best piece of apparatus to use for this purpose is the Lautenschlaeger sterilizer, illustrated on p. 151.

The 1-c.c. pipettes used for the measurement of the water should be plugged with cotton near the end which is placed in the mouth; the pipette should then be placed in a suitable tube containing a cotton plug in its open end, and the whole sterilized.

The author employs cylinders of copper with close-fitting caps, wherein a number of pipettes can be placed during sterilization.

Petri dishes are conveniently sterilized in round copper boxes with tight covers, each box holding six dishes.

**Water samples** for bacteriological examination are most commonly taken in 100-c.c. glass-stoppered bottles. The stopper and neck are covered with tin foil, secured in place by several thicknesses of cotton cloth carefully fastened, and the whole inclosed in a cylindrical copper box and sterilized in the hot-air sterilizer. Samples are also conveniently taken in bulbs of glass with long thin stems, similar to the stock articles in use for specific-gravity determinations. These bulbs can be sterilized by the direct Bunsen flame and sealed while hot. Upon afterward breaking off the point of the stem under water the water will enter the vessel because of the partial vacuum, and the stem can

be at once resealed by using a candle-flame and a blowpipe.

Such bulbs are convenient for taking deep samples, as the point of the stem can be broken by a separate string while the bulb is held by the sinking apparatus.

During transportation, all vessels filled with water samples should be packed in ice, but it is very much better to make the enumeration sowings on the spot, rather than risk changes due to delay.

**Plating for the Total Count.**—Thoroughly shake the sample and transfer 1 c.c. of the water, by means of a sterilized pipette, to a sterile Petri dish. A tube of nutrient

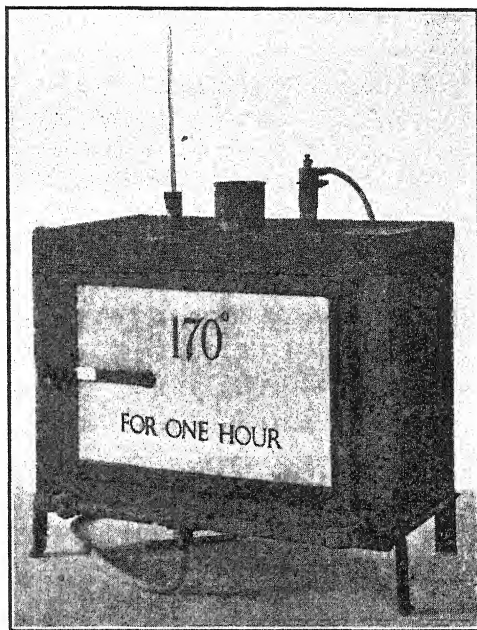


FIG. 13.—Sterilizer for Glassware.



gelatin is liquefied by immersing the tube in warm water at  $35^{\circ}$  to  $40^{\circ}$  C. Having "flamed" the open end of the tube for a moment in the Bunsen flame, the melted jelly is quickly poured into the Petri dish, and mixed with the water by tilting the dish forward and back, after which the dish is placed upon a cool level surface (preferably of stone) for the jelly to set. When the jelly has again hardened the dish should be removed to a moist, dark incubator maintained at a temperature of  $20^{\circ}$  C.

When "agar" is employed, it is melted by immersing its container in a vessel of boiling water, and then allowing the water to slowly cool to  $42^{\circ}$  C. before plating as stated.

To avoid "lumpy" plating it is well to have the Petri dishes warmed to  $42^{\circ}$  C. before pouring the jelly.

Each individual bacterium, finding itself imbedded in material supplying abundance of food, proceeds to surround itself with a multitude of its offspring, until at length the "colony" so produced becomes large enough to be seen by the naked eye. These colonies, each of which corresponds to one original bacterium, are of various sizes. Some of them do, and others do not, liquefy nutrient gelatin. None of them liquefies "agar."

Petri dishes which contain sowings in "agar" should be inverted during incubation to avoid the spreading of surface condensation water. Some workers prefer to employ porous earthenware covers for the Petri dishes. Such covers absorb the water of condensation, but they also tend to dry the medium.

Platings in agar are incubated in both the  $20^{\circ}$  and  $37^{\circ}$  incubators in order to secure a comparison of the growths at the two temperatures.

Should the water contain more than 250 bacteria per cubic centimeter, the volume operated upon should be diminished.

In place of sowing a fraction of a cubic centimeter of water, the "dilution method" should be employed.

One c.c. or 10 c.c. of the water are diluted to 100 c.c. with sterile tap water and then 1 c.c. of the mixture is plated in the usual way. Of course this dilution must be done with great care, as any error is multiplied. Should occasion demand it, a higher dilution should be made.

The dilutions should be made by the use of sterile glass-stoppered bottles and sterile pipettes.

Hill found that

the actual size of the individual colonies increased in proportion as the dilutions rose: i.e., in a plate containing 3,000 colonies, the colonies were very small; in a plate containing half a dozen colonies, the colonies were relatively very large. This suggested that the discrepancy was due chiefly to overcrowding.

If the original sample contains less than 200 bacteria, they will grow in a plate without introduction of those factors of food exhaustion or direct antagonism which we place together under the term overcrowding.

We regard as reliable only the not overcrowded plate, whichever that may be; recognizing it in the fact that the count lies between 40 and 200, ignoring all others, because the standard plate, containing the standard 10 c.c.'s of standard medium, will not support more than about 200 colonies without detriment to the weaker forms.<sup>5</sup>

**Counting the colonies of bacteria** is undertaken forty-eight hours after the plating, when incubation is conducted at 20° C. The agar plates incubated at 37° C. are counted at the end of twenty-four hours.

The maximum or true count naturally would be what

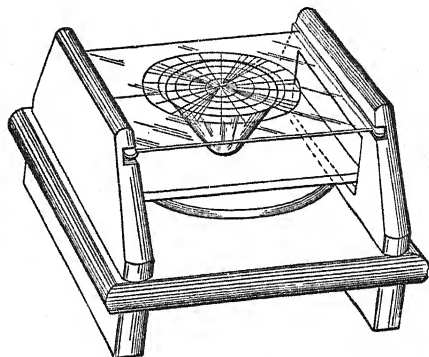


FIG. 14.—Counting Stand.

<sup>5</sup> Hill. H. W., Am. Pub. Health Assoc., 1907, 300.

the student should desire to obtain, if it were practicable to secure it, but some colonies are of such slow growth that necessity demands that he cannot wait for them.

For purposes of comparison in routine work (and usually comparison examinations are the most important form of water investigations) the stated periods will be found the proper intervals between the sowing and the final counting of the colonies.

The counts noted on gelatin at 20° C. and on agar at 37° C., show a difference that is marked.

The higher temperature is fatal to many common water forms, while those of intestinal type are favorably influenced. It must not be assumed that the high temperature count means an accurate enumeration of objectionable organisms, for sundry perfectly harmless bacteria will grow at blood heat; nevertheless there is undoubted value to be derived from a comparison of the two counts in question.

Such irregular results as the following will be noted:

Gelatin at 20° C.	Agar at 37° C.
5,268	495
240	88
37,071	837
121	21
1,400	82
5,283	12
2,033	1,000

---

When the number of the colonies is large, counting must be done with the aid of a ruled glass plate. The best device for this purpose with which the author is familiar is the Miller-McPherson counting apparatus, which needs but little explanation beyond what is given in the illustration on p. 153.

A good and simple modification of this has been made by Caird.

The Wolffhügel device, which is still so commonly em-

ployed, has the disadvantage of not firmly fixing the Petri dish in place, so that there is no small danger of counting the same colonies more than once. Nor is it possible to make use of a Miquel flask as a substitute for the Petri dish, if the Wolffhügel counter be used.

The apparatus is so arranged as to have the ruled glass plate a fixture, while the Petri dish rests upon a movable ebonite plate, which is raised or lowered by the wheel beneath it actuating a hollow screw. The dish thus always may be kept firm against the ruled plate, with no chance of slipping, and moreover it will be always in focus no matter what may be its thickness. The entire plate should be counted.

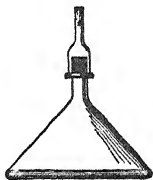


FIG. 15.—Miquel Flask.

The count should be made by the use of a lens magnifying  $3\frac{1}{2}$  diameters. A new binocular form is now on the market.

The count of bacteria per cubic centimeter, although of prime importance for filter testing, is of secondary value for the rating of untreated waters. No hard-and-fast standard of comparison can be given which will prove satisfactory, although sundry have been proposed.

The following is by McWeeney:<sup>6</sup>

Pure water: *Gelatin*, 20° C. Colonies few or many; liquefiers few; chromogenic and slow-growing forms numerous.

*Agar*, 37° C. Sterile or nearly so.

Dirty water: *Gelatin*, 20° C. Colonies at least 500; liquefiers numerous.

*Agar* 37° C. Not to exceed one-tenth of the count on gelatin.

Sewage: *Gelatin*, 20° C. Colonies innumerable; liquefiers many.

*Agar* 37° C. Colonies innumerable; small and gray.

<sup>6</sup> J. Roy. San. Inst., 31, 267.

The number of bacteria per cubic centimeter in water samples taken from the same source at different times will greatly vary with the season and changes in local conditions. Thus the Hudson River water sampled at Troy showed the following variation in bacterial contents during the colder half of the year; similar results for a Rensselaer County spring water are also given.

	Hudson River	Spring
October.....	1,487	158
November.....	626	750
	8,128	
December.....	1,463	1,620
January.....	4,022	2,519
February.....	3,322	166
March.....	....	8,520
April.....	1,343	476
	17,665	

The influence of high water in the river is well shown by the difference between the early and late April samples. Surface washing is the cause of such an increase. The effect of melting snow, and consequent surface washing, is also shown in the March sample of spring water.

In general it may be said that so long as a river is fed by springs, that is, during the hot months, the bacteria tend to remain low in number, but with the advent of floods germ life increases in quantity, because of the washing of the surface of the ground by heavy rainfall and melting snow. During the period when severe frost ties up all surface sources the bacteria again diminish in numbers.

**Differentiation of species**, as has already been stated, must be largely left to writers upon general bacteriology; but a word or two may be properly spent here upon the often broached topic of the recognition of the typhoid bacillus in water, and we should also add a consideration of the tests for and the diagnostic value of the presence of *B. coli*.

Laws and Andrewes in their report to the London

County Council show that the chance of discovering *B. typhosum* in sewage is small. They entirely failed to find it in London sewage.

They examined the sewage flowing (without disinfection) from the Eastern Hospital at Homeston, which received the dejections of forty typhoid patients.

Out of a whole series of samples examined from this latter source only two colonies of *B. typhosum* were differentiated with certainty.<sup>7</sup>

Similar experience was recorded by other observers, and consequently search for the typhoid germ in water became unusual.

Of late, attention has been again directed to this determination, but even though possessing a method of proving with certainty the presence or absence of the typhoid bacterium, such knowledge would not greatly aid.

The information desired is not alone the condition in which a water is to-day, but the chances of its specific pollution to-morrow. In short, to guard against the use of a water which *may* become the carrier of disease organisms even though none be present at the moment of examination.

The situation is tersely summed up by Dr. W. H. Welch:

We possess no satisfactory method for the determination of the presence of the typhoid bacillus in water. With our present methods the most which can be expected from the biological examination of water as regards this question is the determination, not of the actual presence of the typhoid bacterium, but of the possibility or probability of its presence. Our principal guide at present in drawing conclusions as to the possible presence of the typhoid bacillus in suspected drinking water is the recognition of faecal bacteria, and more particularly of members of the colon group.<sup>8</sup> (For definition of colon group see Appendix VI.)

What is sought, therefore, is some index of faecal pollution which will indicate sewage inflow, even though such

<sup>7</sup> Rafter, *Water of Lake Erie*, p. 14.

<sup>8</sup> *J. Am. Pub. Health Assoc.*, xx, 502.

inflow be from sources which for the time being are not pathogenic.

This brings an inquiry regarding the diagnostic value of the "colon group."

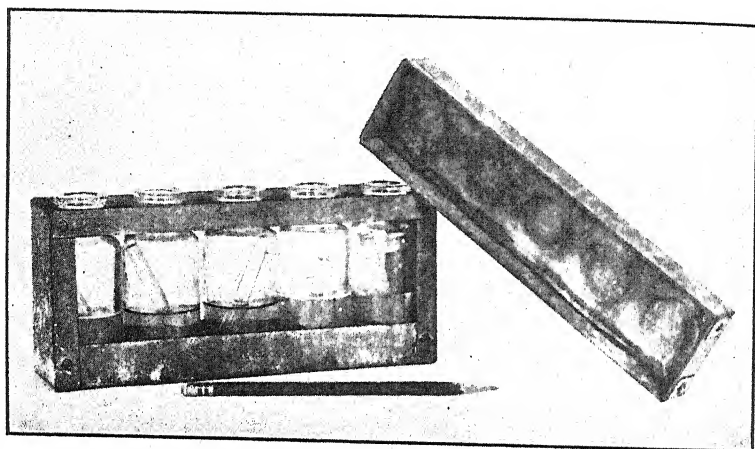


FIG. 16.—Modified Dunham Tubes and Rack Used by the Illinois State Water Survey.

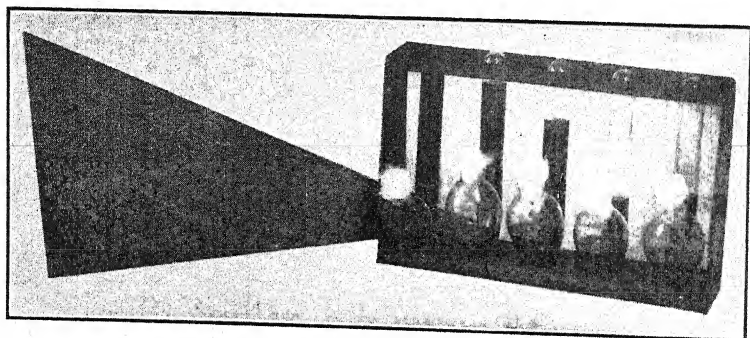


FIG. 17.—Smith Fermentation Tubes.

The *Bacterium coli* has its habitat in the intestines of man and many warm-blooded animals. In small numbers, it is of very wide distribution, and it is doubtful if a surface water could be found that would not furnish it, provided a sufficiently large volume of the water were examined.

Many excellent water supplies derived from upland surfaces would have to be condemned if we were to insist on the absence of *B. coli*.

"Even after storage in open reservoirs, *B. coli* is often present in considerable numbers, owing to the numerous sea gulls that frequent such sheets of water."<sup>9</sup> E. G. Smith<sup>10</sup> has found it upon standing grain. It has also been discovered in the excreta of fish,<sup>11</sup> but that might be accounted for by its presence in the water whence the fish came. Therefore, it is its persistent presence in 10-c.c. samples of a water, rather than its being occasionally found in those of larger bulk, that gives evidence of probable faecal pollution.

It is certainly the author's experience that the colon group is widely distributed, he having found it in waters that a sanitary survey would unquestionably pronounce safe; but it cannot be denied

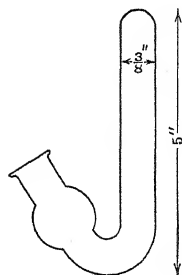


FIG. 18.—Smith Fermentation Tube.

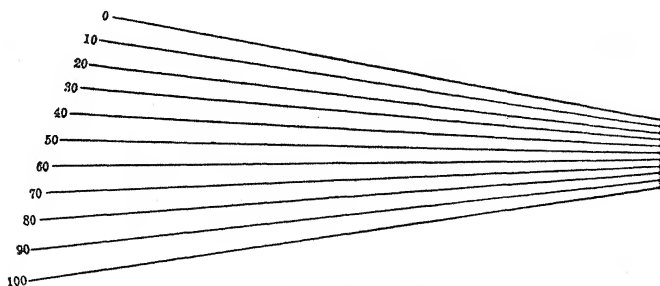


FIG. 19.—Frost Scale.

that its persistent presence in small samples is an indication of pollution that must not be overlooked. Moreover,

<sup>9</sup> J. Roy. San. Inst., xxxi, 269.

<sup>10</sup> Science, xxi, 710.

<sup>11</sup> Hill, Public Water Supplies, p. 28.



the proof of its absence serves to materially aid in formulating an opinion in favor of the purity of a water.

**Tests for *B. coli*.**—1. To each of five (in special cases, ten) fermentation tubes, charged with sterile lactose broth, add 10 c.c. of the water under examination. Mix by tilting the tube, and place in the incubator at 37° C. for forty-eight hours. Fermentation tubes of various forms are in use. They should have a total capacity of about 50 c.c. to accommodate media, sample, and gas.

If any gas-forming bacteria be present, gas will collect in the closed limb of the tube, and some knowledge of the numbers of such organisms present may be gained by observing how many of the tubes show the reaction.<sup>12</sup>

If no gas be formed, *B. coli* is absent. For interpretation of results see Appendix VI.

For more careful search for *B. coli* follow outline on following page.<sup>13</sup>

For the enumeration of organisms not bacterial, in water, Prof. D. D. Jackson has devised a valuable modification of the original Sedgwick-Rafter filter.

The body of the filter is cylindrical and two inches in diameter. The distance from the top to the conical base is nine inches. The small cylindrical prolongation of the cone's apex is two and one-half inches long and one-half inch in diameter.

A perforated rubber stopper, with its hole covered by a disk of fine bolting-cloth, is fitted to the smaller end of the funnel and about three-fourths inch of carefully

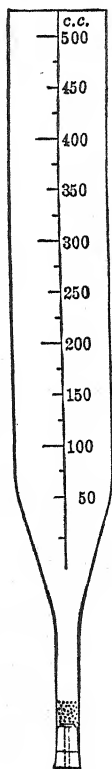


FIG. 20.—Sedgwick-Rafter Funnel (After Jackson).

<sup>12</sup> See the original article by Dr. Theobald Smith in The American Journal of the Medical Sciences, September, 1895.

<sup>13</sup> Extracted from the 1925 report of the committee on Standard Methods.

OUTLINE OF *B. COLI* TEST

Steps in Procedure *	Further procedure required
A. Inoculate lactose broth tubes; incubate 24 hours at 37° C.; observe gas formation in each tube	
1. Gas formation, 10 per cent or more, constitutes positive presumptive test.	
(a) For other than smallest portion of any sample showing gas at this time, and for all portions, including smallest, of sewage and raw water this test is sufficient.....	None
(b) For smallest gas-forming portion, except in examination of sewage and raw water.....	C.
2. Gas formation less than 10 per cent in 24 hours; inconclusive.....	B.
B. Incubate an additional 24 hours, making a total of 48 hours' incubation; observe gas formation.	
1. Gas formation, any amount, constitutes doubtful test, which must always be carried further.....	C.
2. No gas formation, in 48 hours, constitutes final negative test.....	None
C. Make plate from smallest gas-forming portion of sampler under examination after 24 or 48 hours; incubate 18 to 24 hours; observe colonies.	
1. One or more colonies typical in appearance.	
(a) If only "partially confirmed," test is required.....	None
(b) If completed test is required, select two typical colonies for identification.....	E.
2. No typical colonies.....	D.
D. Replace plate in incubator for an additional 18 to 24 hours; then, whether colonies appear typical or not, select at least two of those which most nearly resemble organisms of the coli-aerogenes group.....	E.
E. Transfer each colony fished to:	
1. Lactose broth fermentation tube; incubate not more than 48 hours at 37° C. Observe gas formation.....	None
2. Agar slant; incubate 24 hours at 37° C.	
(a) If gas formed in lactose broth tube inoculated with corresponding culture.....	F.
(b) If no gas formed in corresponding lactose broth tube, test is completed and negative.....	None
F. Make stain, cover slip or slide preparation, and examine microscopically.	
1. If preparation shows nonspore-forming bacilli in apparently pure culture, demonstration of the coli-aerogenes group is completed.....	None
2. If preparation fails to show nonspore-forming bacilli or shows them mixed with spore-bearing forms or bacteria of other morphology.....	G.
G. Replate to obtain assuredly pure culture, select several colonies of bacilli and repeat steps E and F.....	

screened fine sand (between 60 and 100 mesh) is poured into the narrow tube and wet down with distilled water.

From 250 to 500 c.c. of the water under examination are now permitted to filter through the sand. After the water has run through, the sand with the material strained off by it is washed into a test-tube by 5 c.c. of distilled water delivered from a pipette. The organisms, sinking in the test-tube much more slowly than the sand grains, may be decanted, with the water in which they float, into a second test-tube. From this decanted portion, after agita-

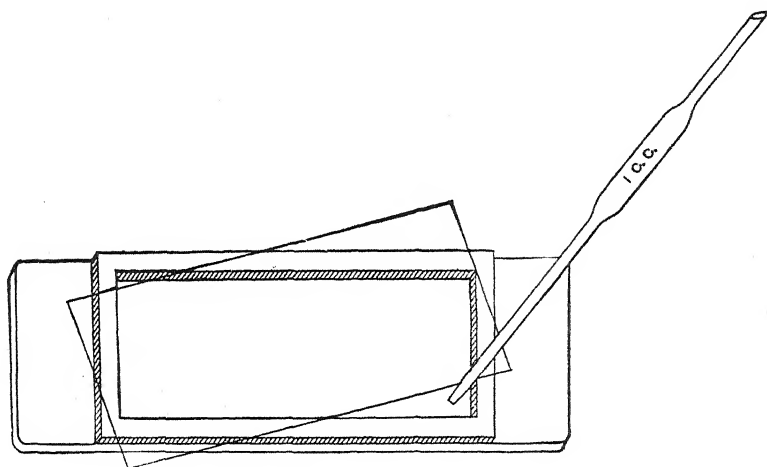


FIG. 21.—Sedgwick-Rafter Counting Cell.

tion, 1 c.c. is delivered by a pipette to the covered "counting cell," which it completely fills.

This excellent device will be found of great service in recognizing and enumerating the various forms of life not bacterial commonly met with in waters.

For purposes of general plankton study, recourse must be had to the writings of biologists who have made such work a specialty. Particularly valuable is a work by Prof. G. C. Whipple, Revised by Prof. Fair and M. C. Whipple, *The Microscopy of Drinking Water*, published by John Wiley & Sons.

## APPENDIX I

### PERMANENT STANDARDS FOR USE IN THE ANALYSIS OF WATER <sup>1</sup>

**Colorimetry** plays such an important part in the analysis of water that standards for comparison are in constant use, and in laboratories for water analysis much time is consumed in the preparation of these standards. At the present writing permanent standards are used for the determinations of color, turbidity, and nitrate. It is proposed to add to this list permanent standards for the determination of ammonia, nitrite, and iron, all of which have been determined heretofore by the use of comparisons made from a series of known amounts of the constituent to be determined, and none of which standards is sufficiently permanent to be used more than once. It may be well to describe the permanent standards already employed, and then to take up in detail the new standards proposed.

#### COLOR

Hazen's platinum-cobalt color standard is designed to fulfill this purpose. It is prepared as follows: 1.246 grams of potassium platonic chloride ( $\text{PtCl}_4 \cdot 2\text{KCl}$ ) and 1 gram of cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) are dissolved in distilled water, 100 c.c. of strong hydrochloric acid added, and the solution made up to 1,000 c.c. with distilled water. If we express the results in parts per million of platinum, this

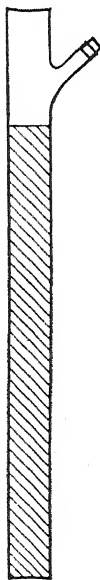


FIG. 22.—Tube  
for Permanent  
Standards  
(After Georgia).

<sup>1</sup>Jackson, Daniel D., Tech. Quart., 13, 320 (1900).

solution is a standard of 500, and standards made by diluting 1, 2, and 3 c.c. of this solution in 50-c.c. Nessler tubes give colors of 10, 20, and 30. Better tubes for this purpose are 100-c.c. tubes of colorless glass 2.2 cm. ( $\frac{7}{8}$ "') in diameter, and 23.5 cm. ( $9\frac{1}{4}$ "') to the 100-c.c. mark. A series of twelve tubes are prepared by adding the following amounts of the standard to the tubes and making up to the 100-c.c. mark with distilled water.

Amount of Strong Standard Added c.c.	Standard Color (Parts per Million Platinum)
0	0
1	5
2	10
3	15
4	20
5	25
6	30
7	35
8	40
10	50
12	60
14	70

Standards beyond this point are difficult of comparison, and waters of deeper color should be read by dilution. The reason for this difficulty is that the components of the color in the natural water are not the same as in the platinum-cobalt standard, and if the depth of the liquid remains the same, the relative absorption of light by these components varies with the strength of the color. The following diagram, Fig. 23, illustrates this point.

Line *A* represents the cubic centimeters of Hazen's standard necessary to make the standards figured at the left if made up in the 100-c.c. tubes described. In this case the cubic centimeters of platinum and of cobalt used are the same. The other lines represent the excess of cobalt solution of the same strength required to match various colored waters, both artificial and natural.

*B* = Maple leaf extract.

*C* = Natural water standard from Fall River, Mass.

*D* = Cedar leaf extract.

*E* = Birch leaf extract.

*F* = Natural water standard from Westboro, Mass.

*G* = Natural water from Winooski, Vt.

Since this diagram was made, a leaf extract and a natural surface water have been examined which follow

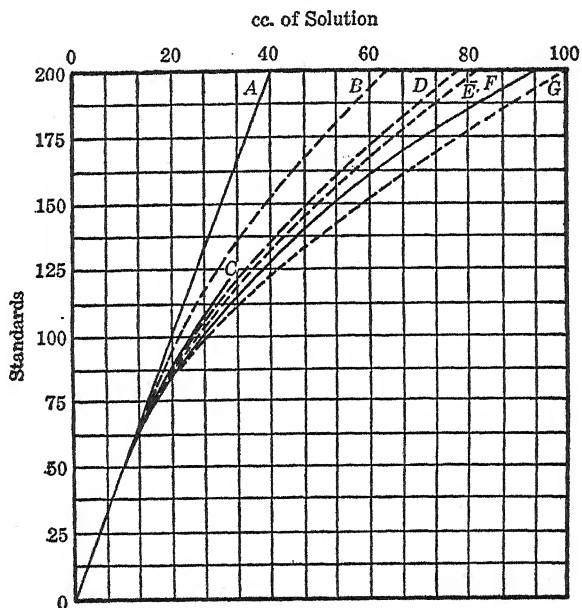


FIG. 23.—Color Curves.

Hazen's standard (line *A*) at 150, and then fall off toward the red (line *B*). The hue of both of these waters was inclined toward the green.

The conclusions to be drawn from this diagram and from the foregoing considerations are:

(1) That if the highly colored waters were uniform in hue, it would be feasible to make standards from two separate solutions of platinum and cobalt to correspond with the diagram, but that it is impossible to make a set of standards which would always

match the color of surface waters because of the difference in hue in various waters, and even in the same water at different seasons of the year.

(2) That while the natural water standards follow more closely the hue usually found in colored waters, they do not agree with each other in hue, if the source of collection is different.

(3) That this failure to agree in hue takes place at about the same point on the scale whether the platinum-cobalt standards or the natural water standards be used.

(4) That above a standard of 70 parts per million of platinum on Hazen's scale, or .90 on the Nessler scale, the color of a water should be read by dilution even when natural water standards are employed.

(5) The Hazen's platinum-cobalt standard if read below 70 is perfectly uniform, and the most practical and accurate standard for the determination of the color in water.

#### TURBIDITY

Professor Mason's permanent standards for turbidity are made by adding a weighed amount of kaolin to distilled water. A series of standards are then prepared which are graduated in parts per million of kaolin. On account of the variation in the size of the particles in kaolin, and the great differences found in different kaolins, it has been deemed advisable to use finely powdered diatomaceous earth instead of kaolin. The diatom frustules being finely striated, break up when ground into particles of great uniformity in size, and are composed of practically pure silica unacted on by water or acids.

This diatomaceous earth is ignited to free it from organic matter, ground to an impalpable powder, put through a 200-mesh sieve to break up the lumps produced in grinding, dried at 100 degrees centigrade, cooled in a desiccator and kept in a tightly stoppered bottle. One gram of this earth is weighed out and put into one liter of distilled water. This mixture equals a standard of 1,000. Twelve dilute standards are prepared in 100-c.c. tubes like those described for color standards, and made up to the 100-c.c. mark in the following manner:

Amount of Strong Standard Added c.c.	Standard Turbidity (Parts per Million Silica)
.0	0
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
4.0	40
5.0	50
6.0	60
7.0	70
8.0	80
9.0	90
10.0	100

These standards are kept tightly corked and are shaken violently before comparison with the water to be measured for turbidity. When new corks are used they are boiled in distilled water several times to extract any coloring matter which they may contain. For higher turbidities the water to be examined is diluted until it falls within the standard scale. The turbidity is always compared side-wise toward the light. For the reading of low turbidities in water similar sets of permanent standards are prepared in bottles of the same size as those employed for collection of the samples of water. Turbidities between 0 and 20 have been found to be determined much more accurately by the use of these bottles.

#### NITROGEN AS NITRATE

A most satisfactory permanent standard for nitrate as determined by the phenol-sulphonic acid method is made up by Mason as follows:

Strong standard nitrate solution is made by dissolving .72 gram of pure potassium nitrate in one liter of distilled water.

Dilute standard nitrate is then made from the strong solution by evaporating 10 c.c. of the strong solution just



to dryness and then adding 2 c.c. of phenol-sulphonic acid, rubbing the residue quickly and thoroughly with the acid by means of a glass rod, and making up to one liter with distilled water.

Permanent standards for comparison are made from this dilute solution in 100-c.c. tubes, 3 cm. ( $1\frac{1}{8}$ "') in diameter, and 13.2 cm. ( $5\frac{1}{4}$ "') to the 100-c.c. mark. Five cubic centimeters of strong ammonia is added to each tube, and the series of standards made up as follows:

Amount of Dilute Standard Added c.c.	Standard Nitrate
.0	.0
1.0	.1
3.0	.3
5.0	.5
7.0	.7
10.0	1.0
15.0	1.5
20.0	2.0
25.0	2.5
30.0	3.0
35.0	3.5
40.0	4.0

If the water to be examined is very low in nitrate, 50 c.c. are evaporated to dryness; 25 c.c. is the usual amount taken, but if the water is high in nitrate less should be used.

If the standards are kept well corked with stoppers which have had the coloring matter extracted from them by boiling water, they will keep perfectly well for several months. Consequently, artificial standards are in this case entirely unnecessary.

#### NITROGEN AS FREE AND ALBUMINOID AMMONIA

The success of Hazen's platinum-cobalt standard for color has led the author to construct tables for the preparation of similar permanent standards for use in the colorimetric determinations of ammonia, nitrite and iron.

The standards which are made up for the determination of ammonia may be duplicated by a permanent set prepared from potassium platonic chloride and cobaltous chloride, and with a little practice the Nessler solution may be prepared to exactly fit the standards each time.

**Preparation of Nessler Solution.**—Dissolve 61.75 grams of potassium iodide in 250 c.c. of redistilled water, and add a cold solution of mercuric chloride which has been saturated by boiling with excess of the salt. Pour in the mercury solution cautiously, and add an amount just sufficient to make the color a permanent bright red. With a little practice the exact depth of color can be easily duplicated. It will take a little over 400 c.c. of the mercuric chloride solution to reach this end point. Dissolve the red precipitate by adding exactly .75 gram of powdered potassium iodide. Then add 150 grams of potassium hydrate dissolved in 250 c.c. of water. Make up to one liter. Mix thoroughly and allow the precipitate formed to settle.

It is best to make up a large amount of Nessler solution, and if by its use the ammonia standards do not fit the artificial ones prepared from the platinum and cobalt solutions, a little more mercuric chloride to increase sensitiveness, or potassium iodide to decrease it, will bring the Nessler solution to the point where, if just 2 c.c. are used, the regular ammonia standards will exactly fit the artificial ones. The artificial standards may then be employed for the ammonia readings until the Nessler solution tested is entirely used up. Of course, each new lot of Nessler solution should be compared to see that it has the proper degree of sensitiveness to fit the standards. Very close to 2 c.c. of Nessler solution should always be used in Nesslerizing, as the amount of this solution affects the depth of color, especially in the lower part of the scale. To prepare the permanent standards two separate solutions are necessary.

**Platinum Solution.**—Weigh out 2 grams of potassium platonic chloride ( $\text{PtCl}_4 \cdot 2\text{KCl}$ ), dissolve in a small amount

of water; add 100 c.c. of strong hydrochloric acid, and make up to one liter.

**Cobalt Solution.**—Weigh out 12 grams of cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), dissolve in distilled water; add 100 c.c. of strong hydrochloric acid, and make up to one liter.

Varying amounts of these two solutions are required, because the color of the Nessler standards becomes more and more reddish as the amount of ammonia increases. The standards are made up in 50-c.c. Nessler tubes 1.7 cm. ( $\frac{11}{16}$ ") in diameter, and 21 cm. ( $8\frac{1}{4}$ ") from the bottom to the 50-c.c. mark. Twelve standards are prepared by filling up to the 50 c.c. mark with distilled water as follows:

c.c. Pt Solution		c.c. Co Solution		Standard Ammonia
1.0	+	.0	=	.0
1.8	+	.0	=	.1
3.2	+	.0	=	.3
4.5	+	.1	=	.5
5.9	+	.2	=	.7
7.7	+	.5	=	1.0
9.4	+	.9	=	1.3
10.4	+	1.3	=	1.5
12.7	+	2.2	=	2.0
15.0	+	3.3	=	2.5
17.3	+	4.5	=	3.0
19.0	+	5.7	=	3.5
19.7	+	7.1	=	4.0
19.9	+	8.7	=	4.5
20.0	+	10.4	=	5.0
20.0	+	15.0	=	6.0

The following diagram, Fig. 24, expresses in an interesting way the relation between the standards and the two solutions used:

It will be seen that very little cobalt is required until the point .7 is reached. Then the cobalt required increases rapidly. It is at about this same point in the Hazen color standards that difficulty in matching begins, because the

deeper colored waters appear more reddish than the standards. But as before stated, in Hazen's color standards the color usually read is so low that standards made from two separate solutions are neither practical nor necessary.

The components of the colors in the natural and in the artificial ammonia standards have not the same appearance at different concentrations, and the same depth. This fact

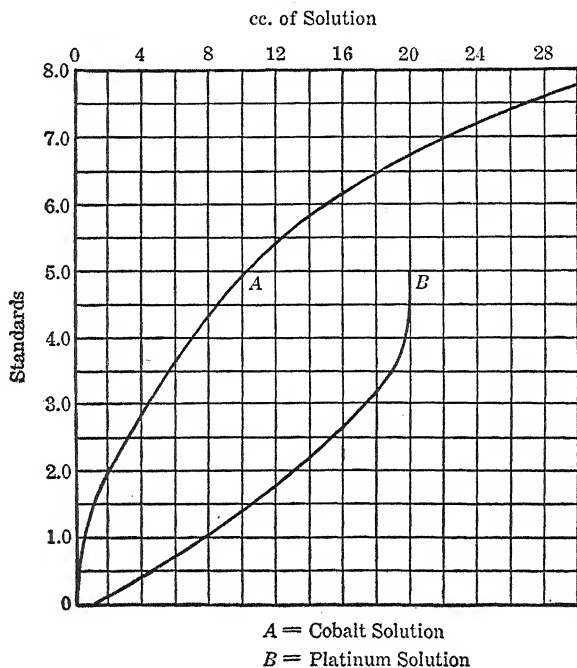


FIG. 24.—Nessler Standards.

may be easily demonstrated by holding the standard of 6.0 sidewise toward the light together with the regular Nessler ammonia standard. While they agree perfectly on examining them lengthwise through the tubes, they do not agree at all sidewise where slight depth is exposed. In this position the artificial standard is decidedly pink, and not brownish yellow as it appears lengthwise. This difference in the coefficient of absorption of light renders it im-

possible to make standards for ammonia from any one single platinum-cobalt solution.

#### NITROGEN AS NITRITE

Standards made from two separate solutions are best in this case also.

**Cobalt Solution.**—Weigh out 24 grams of cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) and dissolve it in distilled water. Add 100 c.c. of strong hydrochloric acid, and make up to one liter with distilled water.

**Copper Solution.**—Weigh out 12 grams of dry cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ); dissolve in water; add 100 c.c. strong hydrochloric acid and make up to one liter with distilled water.

The standards are made up in 100-c.c. tubes like those described for nitrate standards. The following list gives the proportions of each solution to be made up to the 100-c.c. mark:

c.c. Cobalt Solution	c.c. Copper Solution	Standard Nitrite
.0	.0	0
1.1	1.1	1
3.5	3.0	3
6.0	5.0	5
12.5	8.0	10
20.0	8.0	15

The standard of 15, although it can be compared with the nitrite in color, still is not so satisfactory as the others, due to the increased effect of the yellow component either in the copper or the cobalt solution. This it seems, however, cannot in any way be obviated.

If 100 c.c. of water are taken, and on treatment it develops a color corresponding to the standard of 3, then the water contains .003 part per million of nitrogen as nitrite. The following diagram, Fig. 25, shows the proportion of the two solutions used.

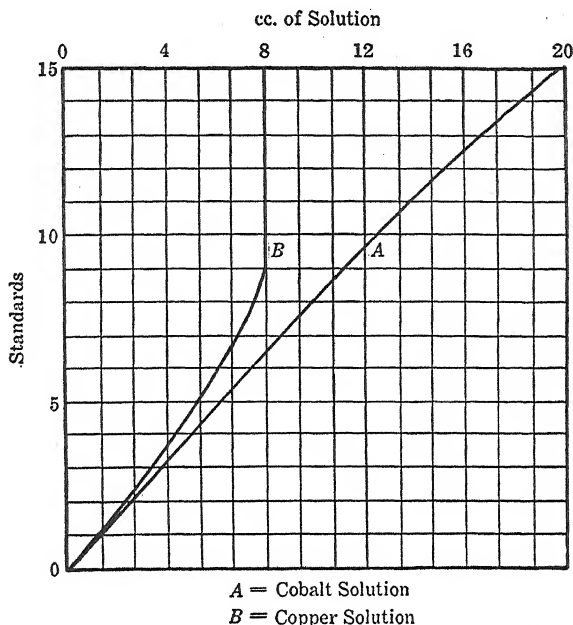


FIG. 25.—Nitrite Standards.

## IRON

Very satisfactory standards for the iron determination may be prepared from platinum and cobalt, but in this case, also, the standards must be made from two separate solutions.

**Platinum Solution.**—Weigh out 2 grams of potassium platonic chloride, dissolve in distilled water, add 100 c.c. of strong hydrochloric acid and make up to one liter with distilled water.

**Cobalt Solution.**—Weigh out 24 grams of dry cobaltous chloride crystals, dissolve in a small amount of water, add 100 c.c. of strong hydrochloric acid and make up to one liter with distilled water.

The standards are prepared in 100-c.c. tubes<sup>2</sup> like those used for nitrate standards, and are made up to the 100-

<sup>2</sup> These iron standards *cannot* be used with *any* other form or size of tube.

c.c. mark with distilled water in the proportions given below:

c.c. Cobalt Solution		c.c. Platinum Solution		Standard Iron
.0	+	0	=	.0
1.0	+	2	=	.1
3.0	+	6	=	.3
5.0	+	10	=	.5
7.5	+	14	=	.7
11.0	+	20	=	1.0
17.0	+	28	=	1.5
24.0	+	35	=	2.0
32.0	+	39	=	2.5
43.0	+	40	=	3.0
55.0	+	40	=	3.5
67.0	+	40	=	4.0

The following diagram, Fig. 26, is interesting as showing the relation of the components used, and the impossibility of matching the higher colors by a single solution.

The brownish red color produced in the determination of iron is unaffected by ordinary variations in temperature. As the color begins to fade soon after it is developed, it is necessary to make the comparisons directly after adding the potassium sulphocyanide solution.

Inasmuch as the amount of each reagent used affects the depth of color obtained in the iron determination, it is necessary to follow very carefully the directions given below.

A known quantity of the water to be tested should be evaporated to dryness, and the *organic matter destroyed by ignition*. The residue is then treated with 5 c.c. of hydrochloric acid (1:1) and heated carefully over a free flame, so that boiling takes place for an instant. The liquid is then washed into a 100-c.c. tube and made up to the 100-c.c. mark with distilled water. Two or three small drops of potassium permanganate solution (5 grams per liter) are added, and the tube is allowed to stand a few minutes.

of permanganate solution, and repeat this until the color becomes permanent and all ferrous iron has been oxidized; 10 c.c. of potassium sulphocyanide (20 grams per liter) are then added, and the liquid thoroughly mixed by pouring

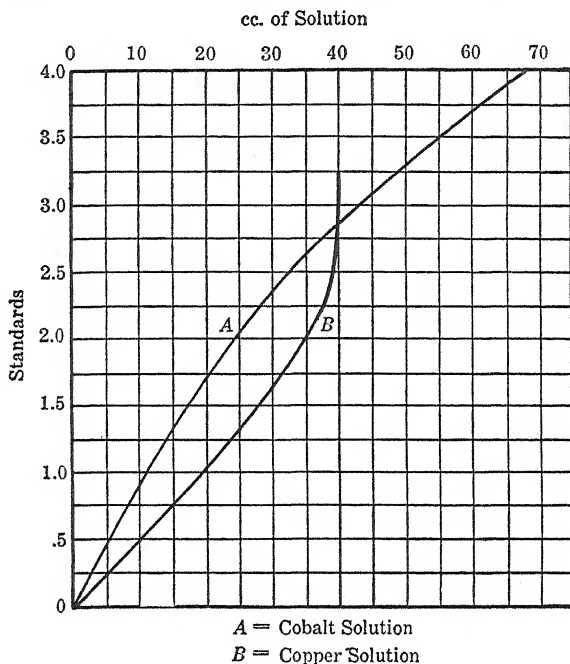


FIG. 26.—Iron Standards.

from one tube into another. If, for example, 100 c.c. of water is taken for evaporation, the figure found by comparison with the standards equals directly parts per million of iron.

#### REFERENCES

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2. *Proc. Am. Chem. Soc.*, **2**, 8.
3. Richards, E. H., and Ellms, J. W., *Jour. Am. Chem. Soc.*, xvii, January, 1896.
4. *Am. Chem. Jour.*, xiv, No. 4.
5. *Examination of Water*, p. 12. John Wiley & Sons.
6. Whipple, G. C., and Jackson, D. D., *Technology Quarterly*,



**PREPARATION OF PERMANENT CHLORINE STANDARD<sup>3</sup>**

The following quantities of copper sulphate and dichromate solutions, which have been prepared in accordance with directions given under Determination of Free Chlorine, when diluted to 100 c.c. and placed in standard 100 c.c. Nessler tubes may serve as semipermanent quantitative standards for the determination of free chlorine by the o-tolidine method. These standards should be checked about every three months by comparing a few of them with freshly prepared standards.

PREPARATION OF PERMANENT STANDARDS FOR FREE CHLORINE

Chlorine (parts per million)	Solution of Copper Sulphate Cubic Centimeter	Solution of Potassium Dichromate Cubic Centimeter
.01	.0	.8
.02	.0	2.1
.03	.0	3.2
.04	.0	4.3
.05	.4	5.5
.06	.8	6.6
.07	1.2	7.5
.08	1.5	8.7
.09	1.7	9.0
.10	1.8	10.0
.20	1.9	20.0
.30	1.9	30.0
.40	2.0	38.0
.50	2.0	45.0

<sup>3</sup> For the original data and for higher free chlorine concentrations the reader should consult the original publication, Ellms, J. W., and Hauser, S. J., Ind. Eng. Chem. 5, 915 (1913).

## APPENDIX II

### PROBLEMS IN INTERPRETATION OF BACTERIAL TESTS

The tabulation of the *B. coli* tests for one year (300 standard samples at five different waterworks) is shown below. How do these supplies rate under the Treasury Department standards? (See p. 186.)

	No. of Samples		<i>B. coli</i> Results
A.....	{ 150	gave	4- 1+
	{ 150	gave	5- 0+
B.....	{ 18	gave	2- 3+
	{ 32	gave	3- 2+
	{ 32	gave	4- 1+
	{ 218	gave	5- 0+
C.....	{ 30	gave	0- 5+
	{ 270	gave	5- 0+
D.....	{ 100	gave	3- 2+
	{ 200	gave	5- 0+
E.....	{ 50	gave	3- 2+
	{ 15	gave	2- 3+
	{ 35	gave	4- 1+
	{ 200	gave	5- 0+
F.....	{ 50	gave	3- 2+
	{ 20	gave	2- 3+
	{ 230	gave	5- 0+

Two samples of water from each of the three following wells were tested for *B. coli*. How should they be rated under the Treasury Department standards?

	No. of Samples		<i>B. coli</i> Results
A.....	2	gave	1+ 4-
B.....	{ 1	gave	1+ 4-
	{ 1	gave	0+ 5-
C.....	{ 1	gave	3+ 2-
	{ 1	gave	0+ 5-

### APPENDIX III

#### SUGGESTED FORMS FOR RECORDING WATER PURIFICATION DATA\*

**SUGGESTED FORMS FOR RECORDING WATER PURIFICATION DATA\***

[illegible]

FIG. 27.—Record Forms.

\*Suggested by American Water Works Association Committee on Purification Data and Forms. J. W. Armstrong, Chairman. J. A. W. W. A., 22, 1665 (1930).

[illegible]

FIG. 28.—Record Forms.

Continuation

## APPENDIX IV

### CONVERSION OF MILLIGRAMS PER KILOGRAM INTO GRAINS PER U. S. GALLON OF 231 CUBIC INCHES

One U. S. gallon of pure water at 60° F., weighed in air at 60° F., at atmospheric pressure of 30 inches of mercury, weighs 58334.94 grains.<sup>4</sup>

Parts per Million	Grains per U. S. Gallon	Parts per Million	Grains per U. S. Gallon	Parts per Million	Grains per U. S. Gallon
1	.0583	36	2.1000	71	4.1417
2	.1166	37	2.1583	72	4.2001
3	.1750	38	2.2167	73	4.2584
4	.2333	39	2.2750	74	4.3167
5	.2916	40	2.3333	75	4.3751
6	.3500	41	2.3917	76	4.4334
7	.4083	42	2.4500	77	4.4917
8	.4666	43	2.5084	78	4.5501
9	.5250	44	2.5667	79	4.6084
10	.5833	45	2.6250	80	4.6667
11	.6416	46	2.6834	81	4.7251
12	.7000	47	2.7417	82	4.7834
13	.7583	48	2.8000	83	4.8418
14	.8166	49	2.8584	84	4.9001
15	.8750	50	2.9167	85	4.9584
16	.9333	51	2.9750	86	5.0168
17	.9916	52	3.0334	87	5.0751
18	1.0500	53	3.0917	88	5.1334
19	1.1083	54	3.1500	89	5.1918
20	1.1666	55	3.2084	90	5.2501
21	1.2250	56	3.2667	91	5.3084
22	1.2833	57	3.3250	92	5.3668
23	1.3417	58	3.3834	93	5.4251
24	1.4000	59	3.4417	94	5.4834
25	1.4583	60	3.5000	95	5.5418
26	1.5167	61	3.5584	96	5.6001
27	1.5750	62	3.6167	97	5.6584
28	1.6333	63	3.6751	98	5.7168
29	1.6917	64	3.7334	99	5.7751
30	1.7500	65	3.7917	100	5.8334
31	1.8083	66	3.8501		
32	1.8667	67	3.9084		
33	1.9250	68	3.9667		
34	1.9833	69	4.0251		
35	2.0417	70	4.0834		

<sup>4</sup> See article by Professor Mason, The U. S. Gallon, in Am. Druggist, January, 1888.

# APPENDIX V

TABLE OF TEMPERATURE CORRECTIONS FOR SPECIFIC GRAVITY OF BRINES

Temp. ° C.	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
P.p.m. Cl	Subtract						Add									
3,000	.0006	.0005	.0004	.0002	.0001	.....	.0002	.0003	.0005	.0007	.0009	.0011	.0013	.0016	.0018	.0020
6,000	.0007	.0006	.0004	.0003	.0001	.....	.0002	.0004	.0006	.0008	.0010	.0013	.0015	.0017	.0020	.0022
12,000	.0008	.0006	.0004	.0003	.0001	.....	.0003	.0005	.0007	.0009	.0011	.0014	.0016	.0019	.0021	.0024
18,000	.0010	.0008	.0006	.0004	.0002	.....	.0003	.0005	.0008	.0010	.0013	.0016	.0019	.0022	.0026	.0029
24,000	.0011	.0009	.0007	.0004	.0002	.....	.0003	.0005	.0008	.0011	.0013	.0016	.0019	.0022	.0026	.0029
30,000	.0012	.0010	.0007	.0004	.0002	.....	.0003	.0005	.0008	.0011	.0014	.0017	.0020	.0024	.0027	.0030
36,000	.0013	.0011	.0008	.0005	.0003	.....	.0003	.0006	.0009	.0012	.0015	.0019	.0022	.0025	.0028	.0031
42,000	.0014	.0011	.0009	.0006	.0003	.....	.0004	.0007	.0010	.0013	.0016	.0019	.0022	.0025	.0029	.0032
48,000	.0015	.0012	.0010	.0006	.0003	.....	.0004	.0008	.0011	.0014	.0017	.0020	.0023	.0026	.0030	.0033
54,000	.0015	.0012	.0010	.0007	.0004	.....	.0004	.0008	.0011	.0014	.0017	.0020	.0023	.0026	.0030	.0033
60,000	.0016	.0013	.0011	.0007	.0004	.....	.0005	.0008	.0011	.0014	.0018	.0021	.0024	.0027	.0031	.0034
66,000	.0017	.0014	.0012	.0008	.0005	.....	.0005	.0009	.0012	.0015	.0018	.0021	.0025	.0027	.0031	.0034
72,000	.0017	.0015	.0013	.0009	.0005	.....	.0005	.0009	.0013	.0016	.0019	.0022	.0025	.0028	.0031	.0035
78,000	.0019	.0015	.0013	.0009	.0006	.....	.0006	.0009	.0013	.0017	.0020	.0023	.0026	.0029	.0032	.0036
84,000	.0020	.0016	.0014	.0010	.0006	.....	.0006	.0010	.0014	.0017	.0020	.0024	.0027	.0030	.0033	.0036

For example on a water containing 36,000 p.p.m. Cl.

Sp. gr. 21 ° C. is found to be 1.0197

Add temperature factor

Sp. gr. at 15 degrees

1.0197

.0619

= 1.0216

## APPENDIX VI

### DRINKING WATER STANDARDS \*

STANDARDS ADOPTED BY THE TREASURY DEPARTMENT, JUNE 20,  
1925, FOR DRINKING AND CULINARY WATER SUPPLIED BY  
COMMON CARRIERS IN INTERSTATE COMMERCE

[Superseding Standard adopted October 21, 1914] <sup>1</sup>

In recommending the adoption of these standards the advisory committee submitted a report discussing the requirements as follows:

#### REPORT OF THE ADVISORY COMMITTEE ON OFFICIAL WATER STANDARDS <sup>2</sup>

The task referred to this committee by the Surgeon General of the Public Health Service is to formulate definite specifications which may be used by the Public Health Service in the administrative action which it is required to take upon the supplies of drinking water offered by common carriers for the use of passengers carried in interstate traffic. The recommendations submitted apply, therefore, only to this special case, and are not proposed for more general application.

Since the purpose of the supervision which the Public Health Service exercises over these water supplies is to safeguard the health of the public, the examinations and specific requirements herein proposed have reference chiefly to forming a judgment of safety, and are designed especially to afford protection against the most serious danger which is associated with water supplies, namely, that of infection with typhoid fever and other diseases of similar origin and transmission. Less emphasis has been placed upon physical and chemical characteristics affecting the acceptability of water with respect to appearance, taste, and odor, because these

\* *Published with the permission of the Surgeon General.*

<sup>1</sup> Public Health Reports, vol. 29, No. 45, Nov. 6, 1914; Reprint No. 232.

<sup>2</sup> Reprint from the Public Health Reports, vol. 40, No. 15, April 10, 1925, pp. 693-721.

are matters of less fundamental importance and because, in actual experience, the water supplies which come under consideration, if satisfactory from the standpoint of safety, will usually be found satisfactory with respect to physical and chemical characteristics.

The first step toward the establishment of standards which will insure the safety of water supplies conforming to them is to agree upon some criterion of safety. This is necessary because "safety" in water supplies, as they are actually produced, is relative and quantitative, not absolute. Thus, to state that a water supply is "safe" does not necessarily signify that absolutely no risk is ever incurred in drinking it. What is usually meant, and all that can be asserted from any evidence at hand, is that the danger, if any, is so small that it cannot be discovered by available means of observation. Nevertheless, while it is impossible to demonstrate the absolute safety of a water supply, it is well established that the water supplies of many of our large cities are safe in the sense stated, since the large populations using them continuously have, in recent years, suffered only a minimal incidence of typhoid fever and other potentially water-borne infections. Whether or not these water supplies have had any part whatsoever in the conveyance of such infections during the period referred to is a question that cannot be answered with full certainty; but the total incidence of the diseases has been so low that even though the water supplies be charged with responsibility for the maximum share which may reasonably be suggested, the risk of infection through them is still very small compared to the ordinary hazards of everyday life.<sup>3</sup>

The committee has, therefore, taken this better class of municipal water supplies as its standard of comparison with respect to safety and proposes, as a fair objective, that the water supplies furnished by common carriers to passengers in interstate traffic be of comparable safety. As regards protection of the traveling public, such a standard is fair, since it implies that the use of the water supplied to them in travel shall not add to the almost neg-

<sup>3</sup> "This evidence actually proves only that the water supplies in question have been generally 'safe' in the past during the period of low prevalence of infection. The likelihood that they will continue to be equally or more safe in the future must, of course, be reckoned from other considerations, such as the probability of future change in the pollution of their watershed, the character and consistency of their protection, etc."



ligible risk which is ordinarily incurred at home by those who habitually use water supplies of somewhat better than average quality. From the standpoint of the carriers also, this standard is believed to be fair and reasonable, since it refers to water supplies which are actually obtainable in all sections of the country and from a great variety of sources.

The next and principal task of the committee has been to set up objective requirements which will conform to this general standard of safety; that is, requirements which will ordinarily be fulfilled by the municipal supplies of epidemiologically demonstrated safety which constitute the standard of comparison, but will exclude supplies of less assured safety. Since there is no single and measurable characteristic of water supplies which bears any known and constant relation to actual safety, the standard recommended is composite, including certain requirements relative to the source and protection of the water supplies in question as indicated by a careful sanitary survey, and certain other requirements relative to bacterial content as shown by standard tests.

It is anticipated that little objection will be raised to the requirements laid down as to source and protection, at least to their general intent, because they are based upon well-recognized principles of sanitary engineering, and because they are necessarily stated in general terms which imply a rather broad consideration of each supply from all angles and the exercise of discretion in forming an ultimate judgment of its fitness. The bacteriological standard, on the other hand, is stated in definite quantitative terms. This is unavoidable if such a standard be included at all, since the methods of bacteriological examinations are quantitative and yield results in the definite terms used in the standard. However, in view of the well-recognized principle that the significance of bacteriological examinations is variable, and must be interpreted with due regard to all other facts known about the particular water supply in question, the objection may be raised that a rigid application of this standard will arbitrarily exclude a considerable number of water supplies which conform to all other requirements and which competent opinion will consider to be quite safe. The validity of this criticism is recognized, but it is not considered of sufficient force to require or justify the lowering of the bacteriological standard proposed. This viewpoint appears proper when it is recognized that the definite terms of bacteri-

ological quality in which this standard is expressed represent only agreement as to safety, and not as to limiting values beyond which demonstrable or even presumptive danger lies. Between the point on which the committee is in agreement as to the assured safety of water supplies and the point at which agreement could be reached as to their dangerous quality is a wide zone. Within this zone lie many water supplies which, if considered in the light of available evidence from all angles, are believed to be as safe as other supplies which conform to all the bacteriological requirements.

The committee, therefore, considers it preferable to recommend that in actual practice the bacteriological standard be applied, as are other requirements, with some latitude; in other words, that supplies which, on rigid inspection, are found to be satisfactory in other respects but fail to meet the bacteriological standard, may be accepted in the discretion of the certifying authority. In view of the character of the personnel intrusted with the responsibility for investigation and administrative action, the committee feels assured that this procedure is preferable to the alternative of rigid and automatic application.

## STANDARDS

### I. AS TO SOURCE AND PROTECTION

(1) The water supply shall be—

- (a) Obtained from a source free from pollution; or
- (b) Obtained from a source adequately protected by natural agencies from the effects of pollution; or
- (c) Adequately protected by artificial treatment.

(2) The water-supply system, including reservoirs, pipe lines, wells, pumping equipment, purification works, distributing reservoirs, mains and service pipes, shall be free from sanitary defects.

NOTE.—1. *Natural agencies* affording more or less complete protection against the effects of pollution are, in surface waters:

Dilution, storage, sedimentation, the effects of sunlight and the associated biological processes tending to natural purification; and, in the case of ground waters, percolation through the soil. Important items in the natural purification of ground water are the character and depth of the strata penetrated.

2. *Adequate protection* by artificial treatment implies that the method of treatment is appropriate to the source of supply; that the works are of sufficient capacity, well constructed, skillfully and carefully operated. The evidence that the protection thus afforded is adequate must be furnished by frequent bacteriological examinations and other appropriate analyses, showing that the purified water is of good and reasonably uniform quality, a recognized principle being that irregularity in quality is an indication of potential danger.

3. *Sanitary defect* means faulty condition, whether of location, design, or construction of works, which may regularly or occasionally cause the water supply to be polluted from an extraneous source, or fail to be satisfactorily purified. (See examples cited in Appendix A.)

An outline of the scope of sanitary survey ordinarily required in the investigation of a water supply to determine whether or not it conforms to these requirements is given in Appendix A.

## II. AS TO BACTERIOLOGICAL QUALITY

(1) Of all the standard (10 c.c.) *portions* examined in accordance with the procedure specified below, not more than 10 per cent shall show the presence of organisms of the *B. coli* group.

(2) Occasionally three or more of the five equal (10 c.c.) *portions* constituting a single standard *sample* may show the presence of *B. coli*. This shall not be allowable if it occurs in more than—

- (a) Five per cent of the standard samples when 20 or more samples have been examined;
- (b) One standard sample when less than 20 samples have been examined.

NOTE.—It is to be understood that in the examination of any water supply the series of samples must conform to *both the above*

requirements, (1) and (2). For example, where the total number of samples is less than six, the occurrence of positive tests in three or more of the five portions of any single sample, although it would be permitted under requirement (2), would constitute a failure to meet requirement (1).

**Definition.**—*The B. coli group* is defined, for the purposes of this test, as in Standard Methods of Water Analysis, American Public Health Association, New York, 1923, and the procedures for demonstration of organisms of this group shall conform to those of the “completed test” as therein specified.

*The standard portion* of water for this test shall be 10 c.c.

*The standard sample* for this test shall consist of five standard portions of 10 c.c. each.

Some general considerations bearing upon the bacteriological standard adopted are discussed in Appendix B, and the quantitative interpretation of fermentation tests is discussed in Appendix C.

### III. AS TO PHYSICAL AND CHEMICAL CHARACTERISTICS

The water should be clear, colorless, odorless, and pleasant to the taste, and should not contain an excessive amount of soluble mineral substances nor of any chemicals employed in treatment.

**NOTE.**—Appropriate tests for the quantitative determination of physical and chemical characteristics are given in Appendix D of this report, together with the values which should ordinarily not be exceeded when these tests are applied. It is not intended, however, to imply that a complete chemical examination, including all these tests, is to be required in the case of every water supply offered. Under ordinary circumstances simple evidence that the water is generally acceptable in appearance, taste, and odor will be considered sufficient; and detailed analysis will be required only when there is some presumption of unfitness by reason of physical or chemical characteristics. Where such analysis shows the presence of lead (Pb), copper (Cu), or zinc (Zn) in excess of the limits specified in Appendix D, this shall constitute ground for

rejection of the supply. Failure of a supply to conform in other respects to the requirements proposed in Appendix D need not be considered ground for rejection unless it be found, on inquiry, that another supply of equal safety and more acceptable physical and chemical characteristics is readily available.

#### APPENDIX A

#### SCOPE OF REQUISITE INFORMATION AS TO SOURCE AND PROTECTION

In order that the administrative authorities may have the necessary information upon which to base their action, it is requisite that each water supply coming under consideration should be carefully studied with reference to its source and protection. The precise scope of such study and of the report thereon will vary according to the circumstances existing in each individual case, and can not be fully specified in any general terms. The general procedure should, however, be substantially as follows:

**1. A Sanitary Survey of the Water Supply Should be Made by a Competent Person.**—The reliability of the data collected will depend largely upon the competence of the person by whom the survey is made, and the careful selection of personnel for this duty is of primary importance. The qualifications which constitute "competence" can not be precisely defined; but, in general, the person making the survey should have received a technical education equivalent to that given in a course in sanitary engineering in a college of engineering or school of public health; should have a broad knowledge of the sanitary features and physical facts concerning water supplies for potable use; and should understand the essential features of water purification plants, their operation and methods of testing.

**2. A Brief General Description of the Water Supply Should be Submitted.**—This should include the name of the owner of the supply and a brief description of sources and catchment areas, of the storage available and of the

plant, with date of installation of main works, and record of subsequent extensions or alterations.

**3. A Brief Summary of the Pertinent Facts Relating to the Sanitary Condition of the Water Supply, as Revealed by the Field Survey, Should be Submitted.**—The following paragraphs will serve to indicate the general scope of the survey. However, not all of the items would be pertinent to any one supply, and in some cases items not in the list would be important.

(A) SMALL GROUND WATER SUPPLIES

Nature of soil and underlying porous strata, whether of clay, sand, or gravel.

Nature of rock penetrated, noting especially existence of limestone.

Depth to strainers.

Slope of water table, as indicated presumptively but not certainly by slope of surface ground.

Nature, distance, and direction of sources of pollution.

Possibility of surface drainage entering the supply.

Methods of protection.

(B) LARGE GROUND WATER SUPPLIES

General character of local geology.

Extent of drainage area likely to contribute water to the supply.

Size and topography of catchment area.

Nature of soil and underlying strata, whether clay, sand, gravel, rock (especially limestone).

Depth to strainers.

Population on the drainage area.

Nature, distance, and direction of local sources of pollution.

Possibility of surface drainage entering the supply; methods of protection.

Methods employed for protecting the supply against pollution, by sewage treatment, waste disposal, and the like.

Protection of collecting well at top and on sides; protection other than check valve or gate against back flow of drain, etc.

Availability of an impure emergency supply.

Use of tile pipes or other conduits not tight where ground water may be contaminated.

Examples of sanitary defects in ground water supplies are caves, sink holes or abandoned borings used for surface drainage or sewage disposal in vicinity of the source. Casing of tubular wells leaky, or not extended to sufficient depth, or not extended above ground or floor of pump room, or not closed at top; or casing improperly used as suction pipe. Collecting well or reservoir subject to back flow of polluted water through improper drain.

Source of supply or structures subject to flooding.

#### (C) SURFACE WATER SUPPLIES, UNFILTERED

Nature of surface geology; character of soils and rocks.

Character of vegetation; forests; cultivated land, etc.

Population and sewered population per square mile of catchment area.

Methods of sewage disposal, whether by diversion from watershed or by treatment.

Character and efficiency of sewage treatment works.

Proximity of sources of fecal pollution to intake of water supply.

Proximity of sources and character of industrial wastes.

Nominal period of detention in reservoir or storage basin.

Probable minimum time required for water to flow from sources of pollution to reservoir and through reservoir to intake.

Shape of reservoir, with reference to possible currents of water, induced by wind, from inlet to water-supply intake.

Measures taken to prevent fishing, boating, swimming, ice cutting, etc.

Efficiency and constancy of policing.

Disinfection of water; kind and adequacy of equipment; duplication of parts; effectiveness of treatment.

Examples of sanitary defects are—

Improper location of intake with respect to bottom of reservoir and current.

Intake exposed and accessible to trespassers.

#### (D) SURFACE WATER SUPPLIES, FILTERED

Size, topography, and surface geology of catchment area.

Population per square mile of catchment area.

Nature of principal sources of pollution, and distance from intake in miles and in time of travel, with special reference to sewered population.

Methods of sewage treatment; effectiveness of process and uniformity of results.

Character of raw water as to turbidity, color, alkalinity, hardness, iron, etc., and as to variations in quality from time to time.

Rated capacity of filter plant in  $\overline{\text{Mgd.}}$ , average water consumption in  $\overline{\text{Mgd.}}$ , rated capacity of pumps.

Capacity of sedimentation or coagulation basins, in  $\overline{\text{Mgd.}}$ .

Number of filter beds, net area of sand surface, effective size of sand, etc.

Coagulation, if any; kind and amount of chemical used.

Aeration, if any; at what point in purification system.

Disinfection, if any; kind and adequacy of equipment.

Storage of filtered water, whether in open or closed basin.

Adequacy of filter control; continuous or part-time attendance.

Frequency and character of analyses of samples of water.



Examples of sanitary defects are—

Existence of by-passes through which unfiltered water may be delivered to the distribution system without proper supervision.

Inadequacy of works, necessitating excessive overloading or by-passing.

Inadequate protection of purified water.

#### (E) PUMPING STATION

Number and capacity of pumps, including reserve; condition of equipment and method of operation.

Examples of sanitary defects are—

Leaky suction pipe.

Pump not self-priming; unsafe water used for priming.

Suction well unprotected from surface or subsurface pollution.

Suction well subject to pollution through back flow of polluted water through drain.

#### (F) DISTRIBUTION SYSTEM

Area and population supplied.

Type of distribution system; whether by gravity, direct pumping, indirect pumping, etc.

Use, location, and capacity of reservoirs and standpipes.

Adequacy of distribution system.

Examples of sanitary defects are—

Existence of cross-connections between primary supply and secondary supply of unsafe quality for fire protection, emergency, or industrial supply.

Return to the system of any water used for cooling, hydraulic operations, etc.

Inadequate protection of distribution reservoir.

Intermittent service, resulting in reduced or negative pressure in distribution system.

New connections of pipe lines joined to the system without prior disinfection of pipes.

Existence of tile or other leaky pipe in distribution system.

Use of lead pipe for house services with water of corrosive quality.

4. *The agent who makes the sanitary survey should submit his personal opinion as to the sanitary character of the supply based on his field survey.*

## APPENDIX B

### THE BACTERIOLOGICAL STANDARD

The bacteriological examinations which have come to be generally recognized as of most value in the sanitary examination of water supplies are—

(1) The count of total colonies developing from measured portions planted on gelatin plates and incubated for 48 hours at 20° C.

(2) A similar count of total colonies developing on agar plates incubated for 24 hours at 37° C. (or in some laboratories incubated 48 hours at 20° C.).

(3) The quantitative estimation of organisms of the *B. coli* group by applying specific tests to multiple portions of measured volume.

Of these three determinations, the test for organisms of the *B. coli* group is almost universally conceded to be the most significant, because it affords the most nearly specific test for the presence of fecal contamination. The committee has, therefore, agreed, after full consideration, to include only this test in the bacteriological standard recommended, believing that neither the 37° C. nor the 20° C. plate count would add information of sufficient importance to warrant complicating the standard by including them in the required examination. The omission of plate counts from the standard is not to be construed, however, as denying or minimizing their importance in routine examinations made in connection with the control of purification processes. On the contrary, the committee wishes

to record its opinion that one or both plate counts are of definite value in such examinations, and to emphasize that it is chiefly in the interest of simplicity that they have been omitted from the standard here proposed.

For the purposes of this standard the *B. coli* group is defined as in the Standard Method of Water Analysis issued by the American Public Health Association, fifth edition, 1923, page 100, namely, "as including all non-spore-forming bacilli which ferment lactose with gas formation and grow aerobically on standard solid media."

In accordance with this definition, it is recommended that the procedure required for demonstration of the *B. coli* group be that prescribed in Standard Methods of Water Analysis for the so-called "completed test," and that this reference be considered to apply to all details of technique, including the selection and preparation of apparatus and culture media, the collection and handling of samples, and allowable intervals between collection and examination. Since the standard procedure cited in this reference does not require differentiation between the various forms or types which are included under the general definition of the *B. coli* group as given above, it has not seemed advisable, in the present state of knowledge, to require such differentiation in the application of this standard.

The principles involved in the quantitative interpretation of fermentation test in multiple portions of equal volume and in portions constituting a geometric series (e.g., 10 c.c., 1 c.c., 0.1 c.c., etc.) are fully discussed in Appendix C. As is therein demonstrated, the testing of multiple portions of equal volume affords a more precise measure of the density of *B. coli* within a relatively narrow range of variation than does the testing of portions in geometric series. Therefore, since the waters which will be offered for certification will, for the most part, represent only a narrow range of moderate pollution, it is required that the examination of each sample shall consist of the

separate testing of five equal portions of 10 c.c. each.<sup>4</sup> There is, of course, no essential reason why the number of portions tested should be five, rather than some larger number, except that it is necessary to limit the labor and materials required, and five portions are considered sufficient for such precision as is ordinarily requisite.

With reference to the total number of samples which must be submitted for examination and the intervals at which they must be collected, it has not seemed practicable to lay down any hard-and-fast requirements. It is obviously desirable, from the standpoint of precision and significance of results, to examine a large number of samples collected at frequent, and preferably at regular intervals. But against the advantages of frequent and regular sampling must be balanced its practical difficulties and the consideration that the number and spacing of samples required depend upon the quality of the supply in question, the nature of its source, and the character and consistency of its protection. For example, less frequent examinations would be required in the case of water from a deep well, apparently exposed to no dangerous pollution and showing no evidence of contamination on occasional examination, than in the case of a supply drawn from a dangerously polluted stream and depending upon consistently maintained artificial treatment for its protection. All that it is considered proper to require, then, as to number and spacing of samples examined is that they shall be sufficient, in the judgment of the certifying authority, to indicate the quality of the supply, with due regard to all facts known as to its source and protection.

In accordance with these principles, the first requirement stated in the standard, namely, that "not more than 10 per cent of all the 10-c.c. portions tested shall show

<sup>4</sup> It is, however, advisable, especially in the examination of waters of unknown quality, or which may be suspected to be highly polluted, to make simultaneous tests in portions of a geometric series, ranging from 10 to .1 cc. or less.

the presence of *B. coli* " may be interpreted as implying that the mean density of *B. coli* shall not exceed about 1 per 100 c.c. The second clause of the standard, which specifies that not more than 5 per cent of samples tested (or not more than one sample if the whole number tested be less than 20) shall show the presence of *B. coli* in three or more of the five 10-c.c. portions, is more complex in its implications and more difficult to explain. It recognizes that, according to the laws of chance, this result would occur in a certain small proportion of the samples tested, even though the mean density of *B. coli* in the whole body of water tested actually remained constant at about 1 per 100 c.c. or less, and consequently that it warrants no inference of actual fluctuations in density unless it occurs with considerably greater frequency than would be expected according to the theory of chance occurrences. A much more frequent occurrence, sufficient to indicate occasional high pollution, is believed, however, to be an omen of potential danger, even though the average quality of the water should be satisfactory (that is, in conformity to the first provision of the standard). This clause of the standard undertakes, therefore, to set a limit to the allowable frequency of positive results in three or more portions of any sample. It is necessary, in so doing, to recognize that water supplies actually do vary in pollution from day to day, and that in many instances the series of tests which will be considered may be small, hence the limit (5 per cent) is set at a frequency which is much higher than might reasonably be expected in a large series of samples from a water in which the actual density of *B. coli* never greatly exceeded 1 per 100 c.c.

In the bacteriological standard which is proposed the committee has undertaken to establish two limiting values to the density of *B. coli*, one limit applying to the mean density as calculated from the entire series of tests made and one to the range and frequency of occasional deviations from this mean. The mathematical principles applied

to the interpretation of fermentation tests with reference to these two limits are discussed in Appendix G, where it is demonstrated:<sup>5</sup>

1. That where 10 per cent of the 10-c.c. portions tested are positive, the most probable density of *B. coli* is about 1 per 100 c.c., subject to a probable error which is proportionate to the number of portions tested.

2. That given this or a lesser mean density, consistently maintained in the water from which the samples are drawn, less than 1 per cent of the samples in a large series would be expected to show *B. coli* in three or more of the five 10-c.c. portions tested.

As to the reasons for specifying these particular limiting values rather than some other values, either higher or lower, it is obvious that the assignment of any definite limits of bacterial content as a criterion of the safety of water supplies of diverse origin and history must necessarily be an arbitrary procedure, because the relation which the determinable bacterial content bears to the actual safety of a water supply is variable and to some extent indeterminate. Therefore, all that may be claimed for the standards proposed is that, in the judgment of this committee, they are reasonable; that is, are consistent with the other requirements specified as to source and protection of the water supplies in question, afford an ample guarantee of safety, and can be met without too costly and burdensome effort.<sup>6</sup>

<sup>5</sup> These demonstrations are, of course, subject to the assumption that the distribution of *B. coli* in the water tested is random, which is an entirely reasonable assumption.

<sup>6</sup> In connection with this last consideration, the committee has analyzed the records of daily examinations of a considerable number of municipal water supplies for the years 1919 to 1922 and finds that a substantial majority of them conform to both requirements of the standard.

## APPENDIX C

## B. COLI DENSITIES AS DETERMINED FROM VARIOUS TYPES OF SAMPLES

By LOWELL J. REED, Ph. D., Associate Professor of Biometry and Vital Statistics, the Johns Hopkins University, School of Hygiene and Public Health

(Prepared by request of the committee in connection with the work of the subcommittee on bacteriological standards)

The fundamental formula for the determination of the probabilities of occurrence of different densities of *B. coli* from the results of any of the usual sampling procedures has been clearly developed in an article by Greenwood and Yule (1) on bacteriological water analysis.<sup>7</sup> The following quotation from this article gives the derivation of this basic formula:

If in the water from which samples of, say, 1 cubic centimeter each are drawn, there exist *B. coli* bacilli in all in a total volume of  $W$  cubic centimeters of water, then, the distribution of bacilli being assumed to be random, the probable numbers of cubic centimeters with 0, 1, 2, 3, — bacilli in each are given by the binomial expansion of

$$\left(\frac{W-1}{W} + \frac{1}{W}\right)^B \quad (1)$$

Since  $B$  and  $W$  are both very large indeed, (1) becomes, by a well-known transformation originally given by Poisson:

$$e^{-\lambda} \left(1 + \lambda + \frac{\lambda^2}{2} + \frac{\lambda^3}{3} + \dots\right) \quad (2)$$

Where  $\lambda = \frac{B}{W}$ . The problem then reduces itself to that of determining the appropriate value of  $\lambda$  and the probable reliability of its determination.

<sup>7</sup> A previous treatment of this problem is that of McCrady (1915). See reference (2) in appended bibliography.

Examination of equation (2) shows that the probability of a sample of 1 c.c. being found to be negative is  $e^{-\lambda}$ . The probability that a sample of  $N$  cubic centimeter will be negative is therefore  $e^{-N\lambda}$ , and that it will be positive is  $1 - e^{-N\lambda}$ . These probabilities must furnish the basis for the solution of any problem of determining *B. coli* densities from the results of sampling processes.

#### SAMPLES IN GEOMETRIC SERIES

The usual test in this country in water examination consists in taking a series of samples the size of which run in geometric progression as, for example, 100, 10, 1, 0.1, and 0.01 c.c. We shall now examine the probable densities of *B. coli* arising from the different cases which may occur in this sampling procedure.

The following solution for the case where the sample shows 100+, 10+, 1-, 0.1-, 0.01-, will illustrate the method of determining the probabilities in any case. For this particular result the probability that the density of *B. coli* falls between the values  $O$  and  $k$  is given by

$$P = \frac{\int_0^k (1 - e^{-100\lambda}) (1 - e^{-10\lambda}) e^{-\lambda} e^{-.1\lambda} e^{-.01\lambda} d\lambda}{\int_0^\infty (1 - e^{-100\lambda}) (1 - e^{-10\lambda}) e^{-\lambda} e^{-.1\lambda} e^{-.01\lambda} d\lambda}$$

$$\begin{aligned} \text{Now } \int_0^\infty (1 - e^{-100\lambda}) (1 - e^{-10\lambda}) e^{-\lambda} e^{-.1\lambda} e^{-.01\lambda} d\lambda \\ = .8100018 \end{aligned}$$

Therefore the probability curve of densities is

$$y = 1.234565 (e^{-1.11\lambda} - e^{-11.11\lambda} e^{-.101.11\lambda} + e^{-111.11\lambda})$$

The cases likely to arise in using the geometric series are as follows:



	100 c.c.	10 c.c.	1. c.c.	0.1 c.c.	0.01 c.c.
(a)	+	-	-	-	-
(b)	+	-	+	-	-
(c)	+	+	-	-	-
(d)	+	+	-	+	-
(e)	+	+	+	-	-

The above cases are listed in order according to the sizes of the most probable density. Cases (b) and (d) are commonly called inconsistencies, but, as will be seen in the following discussion, they lead to as logical curves as do the other cases.

The equations of the probability curves for these cases are as follows:

$$(a) y = 12.344331 (e^{-11.11\lambda} - e^{-111.11\lambda}).$$

$$(b) y = 113.36297 (e^{-10.11\lambda} - e^{-11.11\lambda} - e^{-110.11\lambda} + e^{-111.11\lambda}).$$

$$(c) y = 1.234565 (e^{-1.11\lambda} - e^{-11.11\lambda} - e^{-101.11\lambda} + e^{-111.11\lambda}).$$

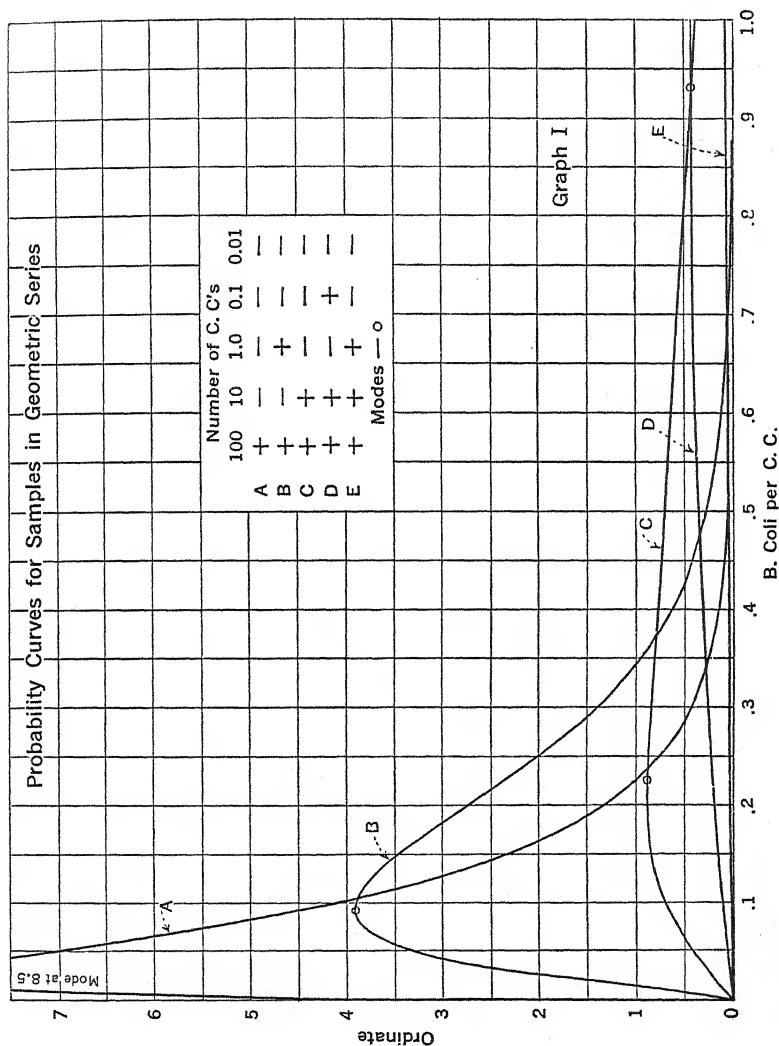
$$(d) y = 12.470554 (e^{-1.01\lambda} - e^{-1.11\lambda} - e^{-11.01\lambda} + e^{-11.11\lambda} - e^{-101.01\lambda} + e^{-101.11\lambda} + e^{-111.01\lambda} - e^{-111.11\lambda}).$$

$$(e) y = 0.1222331 (e^{-.11\lambda} - e^{-1.11\lambda} - e^{-10.11\lambda} + e^{-11.11\lambda} - e^{-100.11\lambda} + e^{-101.11\lambda} + e^{-110.11\lambda} - e^{-111.11\lambda}).$$

The curves of these equations are shown on Fig. 29. The modes for the curves are as follows:

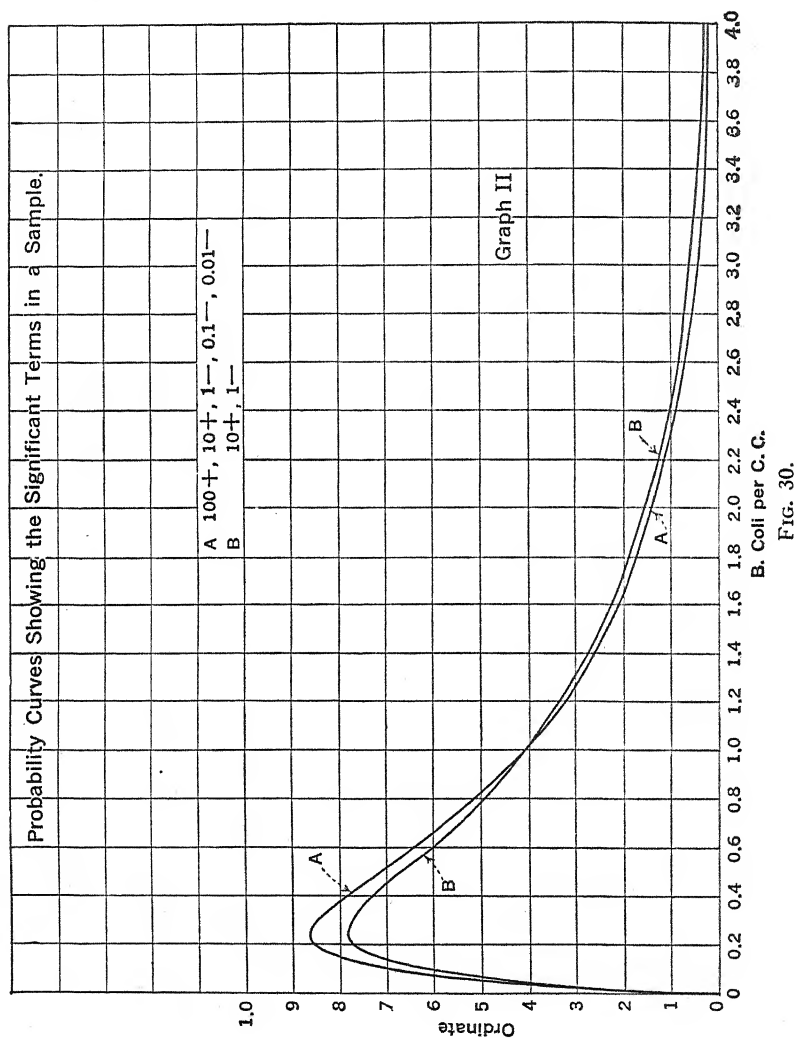
Curve	Mode	Most Probable Number of <i>B. coli</i> per 1,000 c.c. of water
(a)	0.023	23
(b)	.094	94
(c)	.230	230
(d)	.944	944
(e)	2.312	2,312

The rapid change in the modes of these curves shows that the yardstick employed in the case of the geometric



series, for measuring the extent of *B. coli* pollution, has very coarse divisions. For this reason the series is suitable for grading waters that vary widely in the extent of pollution.

Another feature of interest in the geometric series is that the form of the probability curve of densities of *B. coli*, and



the mode of the curve, are almost entirely determined by the two tubes where the results change from + to -. For example, if we have a sample showing 100+, 10+, 1-,

0.1—, 0.01—, and another sample about which our only information is that 10 c.c. is positive and 1 c.c. is negative, curves for the two cases are—

$$y = 1.234565 (e^{-1.11\lambda} - e^{-11.11\lambda} - e^{-101.11\lambda} + e^{-111.11\lambda}).$$

$$y = 1.1 (e^{-\lambda} - e^{-11\lambda}).$$

The forms of these curves are shown on Fig. 30, in which we see that the curves are not significantly different. The mode of the first one is at 0.23027, and of the second at 0.23979. Thus the additional information given by the terms 100+, and 0.1—, 0.01—, has no effect in determining the value of the mode and of its probable error in the case here considered. The same fact holds for all of the consistent cases, and is in harmony with the usual method of interpreting the results of the consistent cases. In the inconsistent cases, however, both changes of sign play a part in determining the most probable pollution and its probable error. These cases are shown on Fig. 29 as intermediate curves between two of the consistent cases, and it would be better to regard them as further subdivisions of the yardstick, having their own appropriate probabilities, than to treat them as inconsistencies.

#### CURVES ARISING FROM FIVE PORTIONS OF TEN CUBIC CENTIMETERS EACH

The proposed standard involves a procedure wherein five tubes of 10 c.c. each are tested. The different types of single samples that may arise are given, with their equations and modes, in the table on the next page.

The case of five positive portions out of five c.c. tested leads to no determination of the probable pollution of the water.

The curves for these equations are shown on Fig. 31.

A comparison of the most probable number of *B. coli* per 1,000 c.c. for these cases with the corresponding terms for the cases that arise in the geometric series method shows

Case	Number of Tubes		Equation of Probability Curve	Mode	Most Probable Number of <i>B. coli</i> in 1,000 c.c.
	Negative	Positive			
a	5	0	$y = 50 e^{-50\lambda}$ . . . . .	0.000	0
b	4	1	$y = 200 e^{-40\lambda} (1 - e^{-10\lambda})$ . . . .	.022	22
c	3	2	$y = 300 e^{-30\lambda} (1 - e^{-10\lambda})^2$ . . . .	.051	51
d	2	3	$y = 200 e^{-20\lambda} (1 - e^{-10\lambda})^3$ . . . .	.092	92
e	1	4	$y = 50 e^{-10\lambda} (1 - e^{-10\lambda})^4$ . . . .	.161	161

that we have in the proposed test a finer subdivision of the scale of pollution. We have, however, shortened our yardstick, so that it is not as suitable for measuring a wide range of pollution as is the geometric series of tests.

A question of greatest importance in determining the method to be used is that of the probable error of the results. In testing tubes of equal size, the most probable pollution and its probable error are easily determined by using the formulæ below. If  $N$  tubes of 10 c.c. each are tested,  $n$  of these tubes giving negative results and  $m$  giving positive results, then the most probable number of *B. coli* per 10 c.c. is given by

$$\lambda = 2.302585 \log \frac{N}{N-m}$$

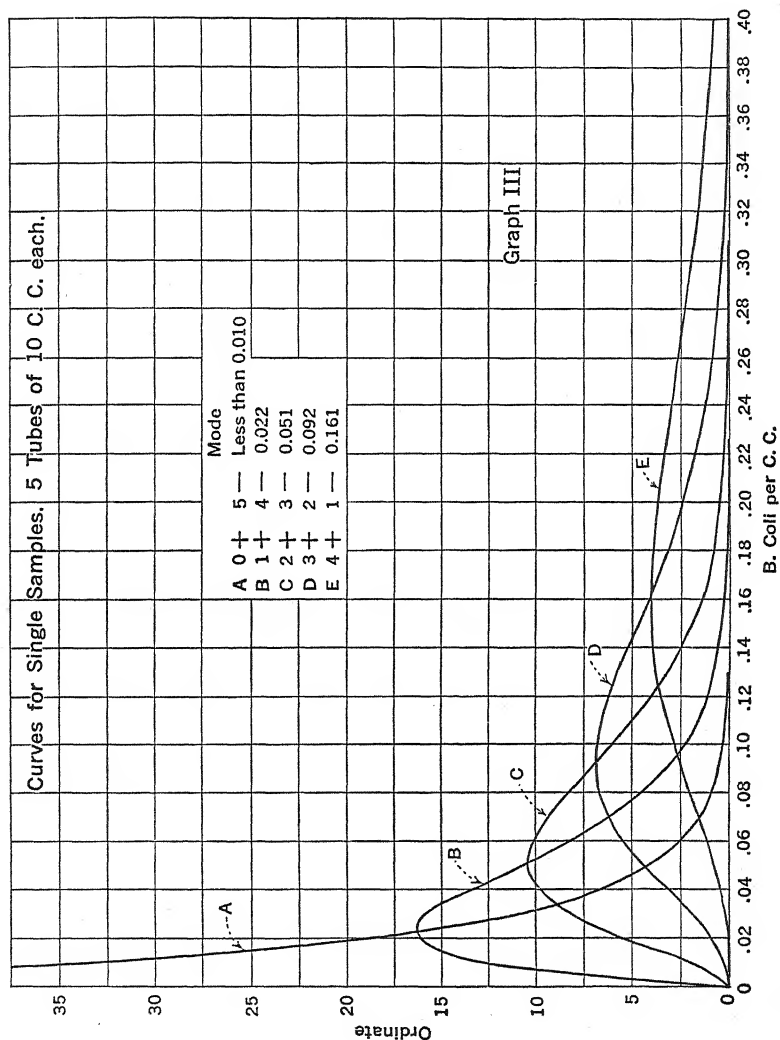
and the probable error of  $\lambda$  is given by

$$P. E. \lambda = 1.553068 \sqrt{\frac{m}{N-n}}$$

These formulæ are given by Greenwood and Yule in the article previously mentioned. Variations of them have been stated by several other writers.

Expressions for the most probable number of *B. coli* per unit of water, and for its probable error, can not be easily

obtained in the case of the geometric series. We may, however, obtain some idea of the relative variability of the two



methods of sampling by comparing single samples in two similar cases. In the case of 1 tube of 10 c.c. positive and 4 tubes of 10 c.c. each negative, the most probable pollu-

tion is 22 *B. coli* per 1,000 c.c. When, in testing by the geometric series, we have 100 c.c. positive and the remain-

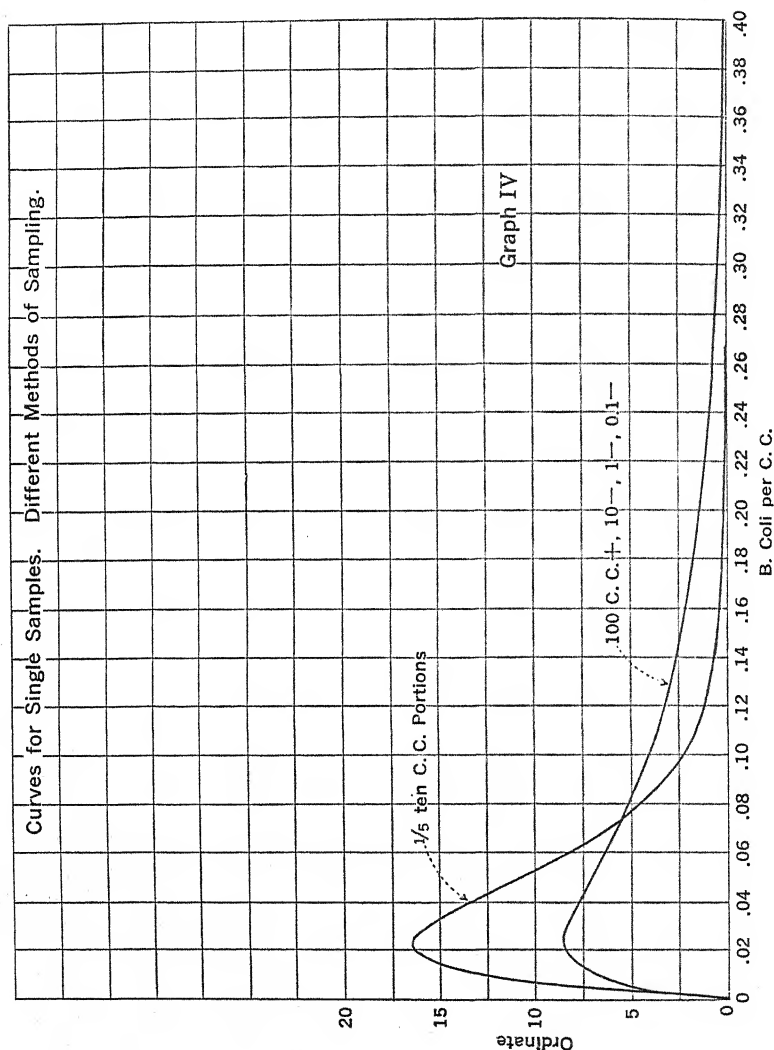


FIG. 32.

der of the portions negative, the most probable number of *B. coli* per 1,000 c.c. is 23. Since the densities are practically identical in these two cases, we may compare

their probability curves to determine which one has the greater variability. Turning to Fig. 32, we see that the two curves have their modes, as stated, at 22 and 23. The curve for the samples taken according to the proposed method is much higher at its mode, and is much less broad in general than is the curve for the samples taken by the geometric series method. Thus the two samples indicate equal degrees of pollution but the probable error to be ascribed to this degree of pollution is much less in the case of the proposed standard of five 10-c. c. portions than in the case of the more commonly used geometric series. This fact may also be brought out by deriving from each curve the probability that the number of *B. coli* per 1,000 c.c. is not greater than 80. For the proposed standard this probability is 0.869, whereas for the geometric series it is only 0.543.

The proposed standard places a limit on the mean pollution and also on the variability. It will, therefore, be of interest to examine both of these factors from the mathematical point of view.

Concerning the mean pollution the standard specifies that not more than 10 per cent of all the 10-c.c. standard portions examined shall show the presence of organisms of the bacillus coli group. For this limiting value we have the following equation expressing the probability that the water is polluted to any specified degree.

$$Y = A(e^{-90\lambda} - e^{-100\lambda}) \frac{N}{10}$$

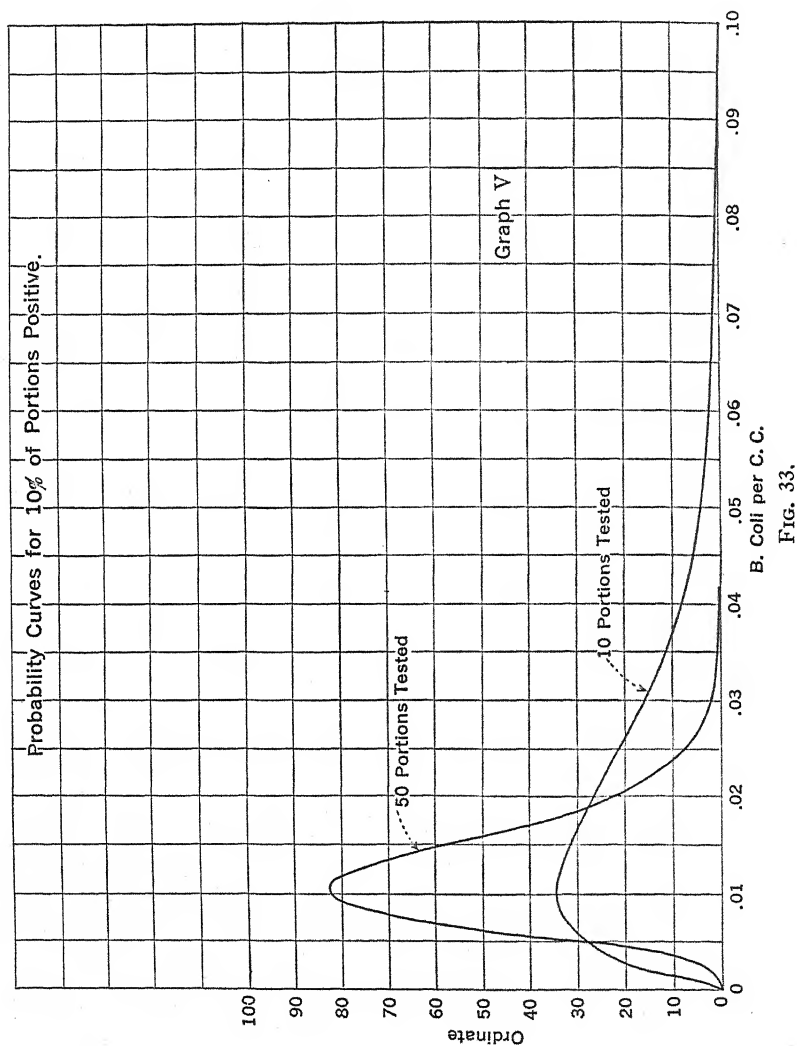
where

$$A = \frac{1}{\int_0^{\infty} (e^{-90\lambda} - e^{-100\lambda}) \frac{N}{10} d\lambda}$$

and  $N$  is the total number of portions tested. The curves for the cases,  $N=10$ , and  $N=50$ , are plotted on Fig. 33. Most of the characteristics of this probability curve depend



upon  $N$ . The position of the mode, that is, the most probable value of the pollution, is, however, independent of  $N$ ,



with a value of 10.5 *B. coli* per 1,000 c.c. This means that, when 10 per cent of the portions tested are positive the most likely pollution of the water is that expressed

by a density of 10.5 *B. coli* per 1,000 c.c., or 1.05 per 100 c.c.

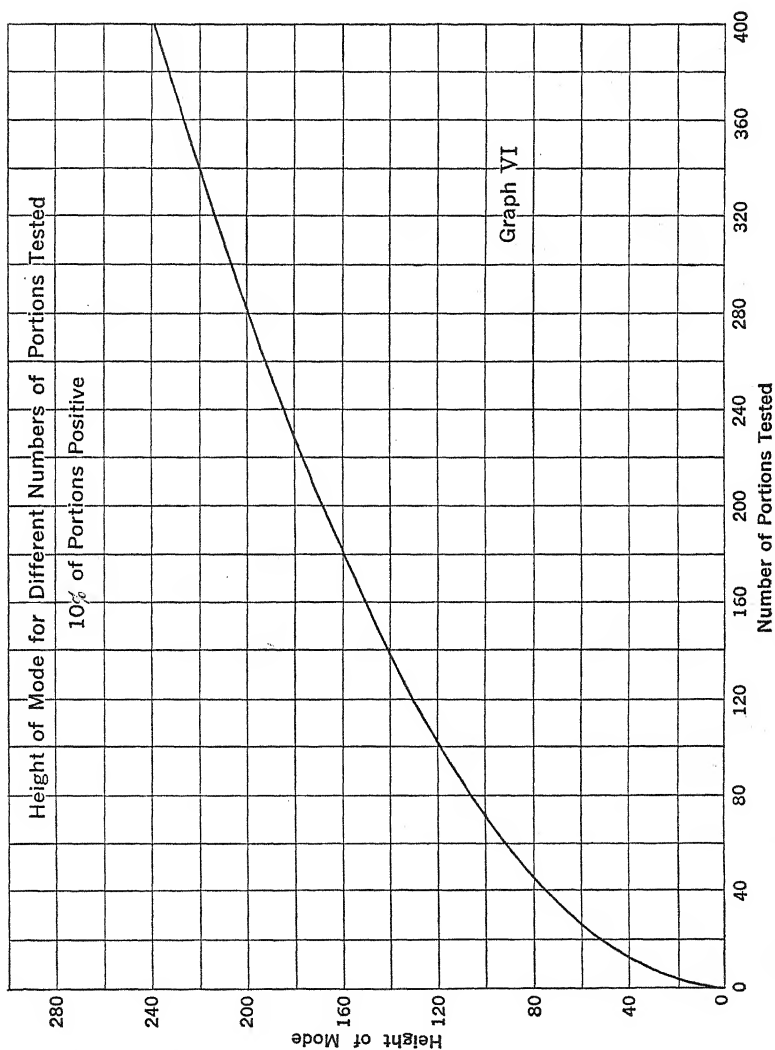


FIG. 34.

Although the position of the mode is independent of  $N$ , the height of the ordinate at the mode is not. This ordinate is a measure of the reliability of the predicted value of the

density, the reliability increasing as the ordinate increases. The relationship between this ordinate and  $N$ , the number of portions, is shown on Fig. 34. The curve indicates that it is well to have at least 100 portions in order that we may be out of the region of sharpest increase on this curve.

Another view of the increase in the reliability of the determination of the pollution with increasing  $N$  may be obtained by examining the distributions for the two cases shown on Graph V. It will be seen that the curve for  $N=10$  is much more widely spread than is that for  $N=50$ .

Considering variability from another point of view, we may ask the following question: Assuming that the density of *B. coli* remains constant at the maximum limit set by the standard (10.5 *B. coli* per 1,000 c.c.), with what frequency should we expect to obtain, on the basis of simple sampling, the different results which may arise in a sample consisting of 5 portions of 10 c.c. each? Since the probability that a portion of 10 c.c. will be negative is given by  $e^{-10\lambda} = 0.9$ , the required frequencies are given by the expansion of the binomial  $(0.9+0.1)^5$ . These frequencies are shown in the following table:

Number of + Portions in Sample (5 Portions)	Per Cent of Samples Having Specified Num- ber of + Por- tions	Per Cent of Samples Having Specified Num- ber of + Por- tions or More
0	59.049	100.000
1	32.805	40.951
2	7.290	8.146
3	.810	.856
4	.045	.046
5	.001	.001

This table furnishes the basis of the second part of the proposed standard. We see that under the above assumption only 0.856 per cent of a given series of samples should by chance show three or more positive portions. The pro-

posed standard specifies 5 per cent for this condition, thus allowing more variability than would be expected to arise from simple sampling.

## APPENDIX D

### THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF ACCEPTABLE WATER SUPPLIES

#### DEFINITION OF A SATISFACTORY WATER

With respect to chemical and physical characteristics a water, to be suitable for drinking and culinary purposes on common carriers engaged in interstate traffic, should be clear, colorless, odorless, pleasant to the taste, should be free from toxic salts, and should not contain an excessive amount of soluble mineral substances, nor of any chemicals employed in treatment.

#### QUANTITATIVE DESCRIPTION <sup>8</sup>

In the quantitative description of acceptable supplies which follows, the values given are intended to represent the maximum which is considered to be ordinarily allowable in the water supplies to which this report refers. It is realized that in many localities supplies of water are available which do not approach the limits allowed here; and in such cases the best available supply should be used.

All values given in the following descriptions are in terms of parts per million, by weight, excepting values for turbidity and color, which are expressed in the arbitrary scales which are in general use. A statement of the methods of analysis recommended for the determination is given in each instance.<sup>9</sup>

<sup>8</sup> Regarding the proposed application of the physical and chemical standards in the examination and certification of water supplies offered, see "note" in text of Requirement III, p. 187.

<sup>9</sup> For the chemical determinations referred to in this report, the methods of analysis recommended by the Association of Official Agricultural Chemists are

## PHYSICAL CHARACTERISTICS

1. **Turbidity** should not exceed 10 (silica scale) and in general it should not be more than 5.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 4.<sup>9</sup>

2. **Color** should not exceed 20 (standard platinum-cobalt scale) and preferably should be less than 10.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 8.<sup>9</sup>

3. There should be *no odor* of hydrogen sulphide, chlorine, or other substance; and the water should be free from odors caused by the presence of microscopic organisms.

CHEMICAL SUBSTANCES WHICH MAY BE PRESENT  
IN NATURAL WATERS

1. **Lead (Pb)** shall not exceed 0.1 part per million and *Copper* (Cu) shall not exceed 0.2 part per million.

Preliminary test (Hanford and Bartow's Method):

To 100 c.c. of the water add 2.0 grams of pure crystalline ammonium chloride, 2 c.c. of acetic acid, and 2 or 3 drops of a 10 per cent solution of sodium sulphide. One or two cubic centimeters of hydrogen sulphide water may be substituted for the sodium sulphide solution if desired. Compare immediately in Nessler jars with standards prepared by adding known amounts lead nitrate to distilled water diluting to 100 c.c. and treating as directed for the sample. Standards should contain 0.01, 0.02, 0.03 milligram of lead (Pb). The method is sufficiently accurate when less than 0.3 part per million lead or copper is represented.

If it is desirable to determine the amount of the metals with greater accuracy, the following methods are recommended:

satisfactory and may be substituted for those recommended by the American Public Health Association, which are specifically cited.

Lead (Pb): Standard Methods of Water Analysis, American Public Health Association, 1923, page 53.

Copper (Cu): Standard Methods of Water Analysis, American Public Health Association, 1923, page 55.

2. **Zinc (Zn)** shall not exceed 0.5 part per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 54.

3. **Sulphate (SO<sub>4</sub>)** should not exceed 250 parts per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 65.

4. **Magnesium (Mg)** should not exceed 100 parts per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 65.

5. **Total solids** should not exceed 1,000 parts per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 25.

6. **Chlorides (Cl)** should not exceed 250 parts per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 42.

7. **Iron (Fe)** should not exceed .3 part per million.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 46.

#### CHEMICAL SUBSTANCES WHICH MAY BE PRESENT IN OVERTREATED WATERS

1. The water should contain *no caustic alkalinity*.

Methods: Based on determination of alkalinity, Standard Methods of Water Analysis, American Public Health Association, 1923, page 34.

2. The water should have *no odor or taste of free chlorine*.

3. The water should contain a residual alkalinity of at least 10 parts per million if it has been treated with sulphate of aluminum or other aluminum compound.

Methods: Standard Methods of Water Analysis, American Public Health Association, 1923, page 32.

4. *The carbonates of sodium and potassium*, taken together and calculated as normal calcium carbonate, should not exceed 50 parts per million.

Methods: Based on determination of alkalinity, Standard Methods of Water Analysis, American Public Health Association, 1923, page 34.

#### DISCUSSION

It is obvious that a water which is turbid, or colored to a degree which is easily noticeable, or which has an unpleasant or unusual odor or taste, will be looked upon with suspicion by the passengers and employees to whom it is served for drinking purposes, and that for this reason its use should not be permitted where clarification is practicable or where a more acceptable supply is available.

The presence of considerable amounts of calcium and magnesium salts makes the water unpleasant to use for washing, and also for drinking, to persons who have been accustomed to softer water, although, on the other hand, persons who are accustomed to the harder waters may find the softer waters less agreeable to their taste. While it is open to question whether it would be justifiable to require the dilution of hard water by distilled water in order to keep within the limits specified herein, it would be proper to require carriers to select the local supplies which most nearly fulfill the requirements of the standards with respect to mineral content.

In so far as the chemical composition of the water may cause inconvenience by its irritating effect upon the intestinal canal, or by any more serious effect upon well-being, the certifying authority will be justified in demanding that due regard be paid to the matter by common carriers. Unfortunately, it is difficult to secure reliable information concerning the physiological activity of salts as found in waters. Idiosyncrasy is important. It is universally ad-

mitted, of course, that poisonous metals such as lead and copper should not be allowed in water for drinking or culinary purposes, but the difficult points are concerned with the less poisonous substances, or salts which are normally present. The effect of sulphates, especially of magnesium sulphate, is, however, well recognized, and it would be desirable to avoid the use of waters in which the concentration of these salts is sufficiently high to be annoying.

Where waters are treated with chemicals in order to soften them, or to purify them in any way, it is desirable that any excess of the chemicals used shall be avoided. Caustic alkalinity from excess of lime, more than a trace of the aluminum compounds added, or free chlorine, are objectionable in the effluent from a purification plant.

In general, it is considered proper to insist that the effort should be made to find waters which are as satisfactory as possible from the standpoint of chemical characteristics but with due regard to the region within which the supply must be obtained.

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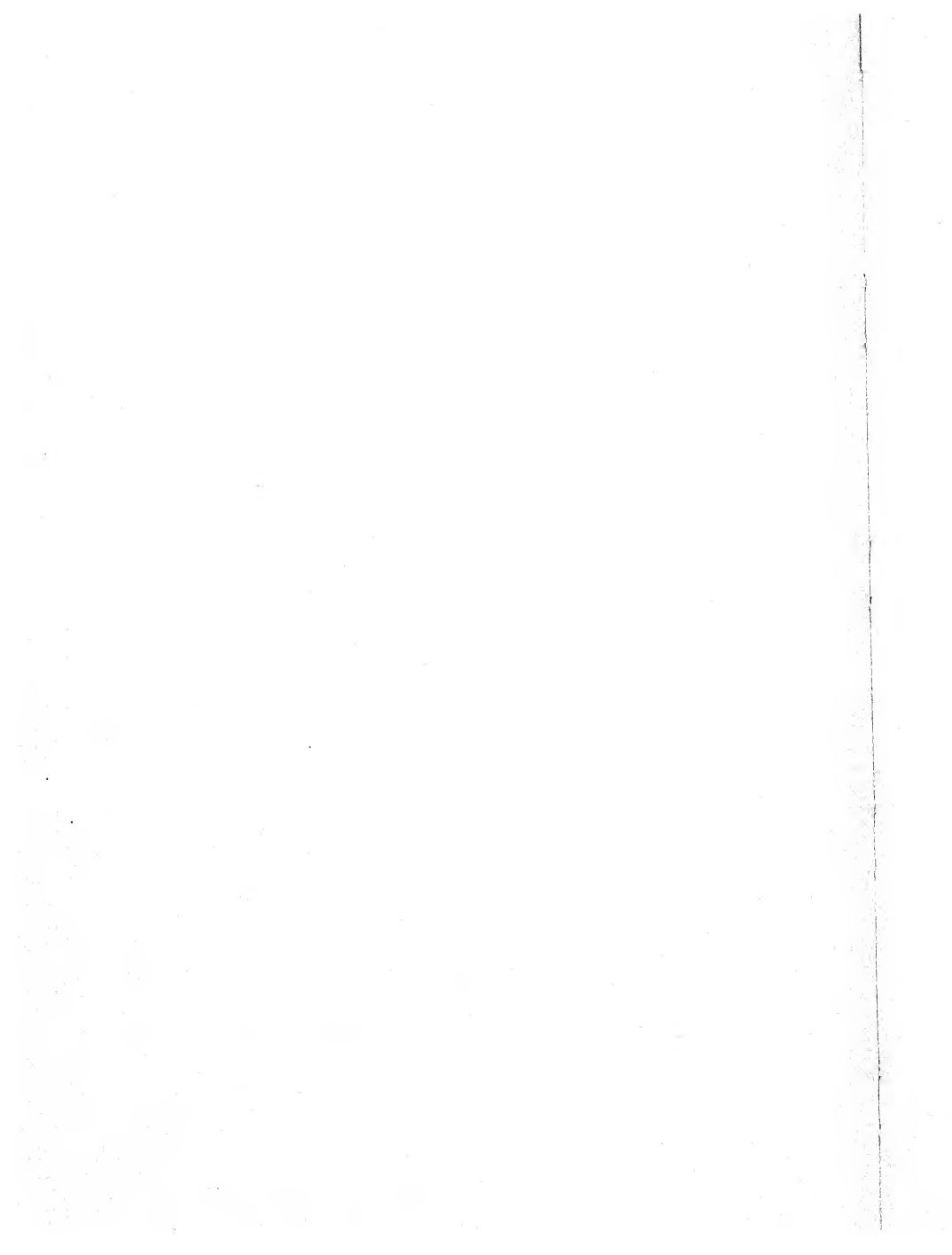
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